

# Final Report on Computational Reacting Gas Dynamics

NASA Grant NAG-1-726

S. H. Lam

Department of  
Mechanical and Aerospace Engineering  
Princeton University  
Princeton, N.J. 08544, U.S.A.

January 25, 1993

## Abstract

This is the final report of NASA Grant NAG-1-726. The method of *Computational Singular Perturbation* (CSP) for simplified kinetics modeling was developed under this grant monitored by Dr. Peter Gnoffo of NASA Langley Research Center, Hampton, VA. The grant period is November 14, 1986 to January 31, 1993.

## 1 Introduction

In the study of high speed flows at high altitudes, such as that encountered by re-entry spacecrafts, the interaction of chemical reactions and other non-equilibrium processes in the flow field with the gas dynamics is crucial. Generally speaking, problems of this level of complexity must resort to numerical methods for solutions, using sophisticated computational fluid dynamics (CFD) codes. The difficulties introduced by *reacting gas dynamics* can be classified into three distinct headings:

- I. The usually inadequate knowledge of the reaction rate coefficients in the non-equilibrium reaction system, and
- II. The vastly larger number of unknowns involved in the computation and the expected *stiffness*<sup>[1]</sup> of the equations, and
- III. The interpretation of the detailed reacting CFD numerical results.

It is not uncommon to have to deal with reaction systems involving tens of reactants which participate in hundreds of elementary reactions (using speculative rate coefficients) which have vastly disparate *time scales*. Assuming that sufficient computing resources are available, that the most up-to-date reaction rate coefficients have been used, we must still address item #III above: how does one extract physical understanding from the massive amount of numerical results generated by a validated reacting CFD code?

Traditionally, an important component of a theory is its *formulation*. By limiting its validity on some specific domain of the parameter space, a traditional theoretician “neglects” the unessential complications and retains only the barest mechanisms to arrive at the *simplified model* which nevertheless fully mimics the behaviors of the complete *full-model*. In most cases, it is the simplified model itself, rather than the detailed (analytical or numerical) solution of the simplified model, that offers the most physical insights to the problem under investigation. This traditional approach is distinctly different from the modern CFD approach: retain all complications which can be overcome by massive computing resources; just generate the numerical solutions, then worry about what physical insights can be extracted from the solutions later.

The research performed under this grant accepts the premise that reacting flows of practical interest in the future will in general be too complex or

“untractable” for traditional analytical developments. The power of modern computers must be exploited. However, instead of focussing solely on the construction of numerical solutions of full-model equations, attention is also directed to the “derivation” of the *simplified model* from the given full-model. In other words, the present research aims to utilize computations to do tasks which have traditionally been done by skilled theoreticians: to reduce an originally complex full-model system into an approximate but otherwise equivalent simplified model system. The tacit assumption is that once the appropriate simplified model is derived, the interpretation of the detailed numerical reacting CFD numerical results will become much easier.

The approach of the research is called *computational singular perturbation* (CSP)<sup>[2]</sup> which is developed under the present grant. Dr. D. A. Goussis, currently assistant professor at University of Patra in Greece, was a research staff member and made significant contributions to the work reported here.

## 2 Goals of the Research

The traditional approach to derive simplified kinetics models uses the so-called *steady-state* and *partial-equilibrium* approximations<sup>[3],[4],[5],[6],[7],[8]</sup>. The steady-state approximation is applied to certain “radicals” or “reaction intermediaries,” and the partial-equilibrium approximation is applied to certain “fast” reactions. For relatively simple and therefore “tractable” reaction systems, these approximations are applied guided by experience and intuition. The results of such analytical studies is a “reduced” reaction system. The concentration of the radicals can be found from a set of algebraic equations of state derived from the approximations, enabling the reduction of the number of unknowns. The simplified kinetics equations derived is no longer stiff. Most importantly, much insight can be gain from inspecting the equations of state and the simplified kinetics equations. Usually, once an analytical simplified model is obtained, the following list of questions can be answered intelligently by inspection of the results.

1. How many algebraic “equations of states” are available and what are they?
2. How many “conservation laws” are available and what are they?

3. What reactions are so fast that their reaction rate coefficients need not be known accurately so long as they are sufficiently fast?
4. What reactions are so slow that they can be ignored altogether?
5. What reactions are primarily responsible for the current behavior of the solution?
6. What is the effective stoichiometry of the reaction system?
7. Which reactants can be solved for in terms of the others from the available equations of state?
8. What reactants can be summarily excluded from the reaction system?
9. What is the response of the reaction system to some perturbation?

Given a massively complex chemical reaction system involving  $N$  unknowns and  $R$  elementary processes where  $N$  and  $R$  are large numbers, the traditional approach is not viable. The goal of the present research is to generate the simplified model and the answers to the above questions using numerical computations.

### 3 Example

Consider a simple reaction system with three species  $A$ ,  $B$  and  $C$  and two elementary reactions:

Reaction #1



Reaction #2



The two unknowns can be considered the components of a column vector  $\mathbf{y} = [A, B]^T$ . The *stoichiometric vectors*  $\mathbf{s}_r$  and *reaction rates*  $F^r$  of the elementary reactions are expressed as follows:

$$\mathbf{s}_1 = [-2, 1, 0]^T, \quad F^1 = k_1(A^2 - K_1 B), \quad (3.3)$$

$$\mathbf{s}_2 = [-1, 1, 1]^T, \quad F^2 = k_2(A - K_2 BC), \quad (3.4)$$

where  $k_1$ ,  $k_2$ ,  $K_1$  and  $K_2$  are rate coefficients obtained from up-to-date and reliable databases. The governing equations can be written as:

$$\frac{dy}{dt} = s_1 F^1 + s_2 F^2. \quad (3.5)$$

Now suppose it is known that reaction #2 is very fast and becomes *exhausted* very quickly. How does one take advantage of this observation to derive the simplified model equations?

Obviously, when reaction #2 is exhausted, one would have:

$$F^2 = k_2(A - K_2 BC) \approx 0 \quad (3.6)$$

which is an algebraic *equation of state* relating  $A$ ,  $B$  and  $C$ . However, it is easy to verify that if one substitutes (3.6) back into (3.5), one would obtain the **wrong** answer for the simplified model equations. The difficulty of this simple-minded but incorrect derivation is quite subtle but is widely known. Consequently, special *ad hoc* procedures are recommended by various authors on how to proceed once the fast reactions of a reaction system have been identified. A common feature of these *ad hoc* procedures is that the unknowns are divided into two groups: those which can be eliminated from the differential equation system by the use of the derived equations of state, and those which cannot. The first group is usually called *radicals* or *intermediaries*. For the example here, a knowledgeable kineticist will correctly conclude that either  $A$  or  $B$  can be treated as radicals, while  $C$  cannot.

Normally, a chemical reaction system respects the Law of Conservation of atomic elements. While such conservation laws are obviously automatically satisfied by a correctly formulated model, their existence is usually identified on physical grounds rather than on mathematical grounds. For the present example which is hypothetical, the physical identification of such laws become impossible. However, it can readily be verified mathematically that  $A + 2B - C$  is the only *conserved scalar* for this reaction system.

We can represent (3.5) by the following *alternative representation*:

$$\frac{dy}{dt} = s_{1'} F^{1'} + s_{2'} F^{2'} \quad (3.7)$$

where the primed reactions are some linear combination of the original elementary reactions:

Reaction #1'

$$\mathbf{s}_{1'} = \mathbf{s}_1 - c\mathbf{s}_2, \quad F^{1'} = F^1, \quad (3.8)$$

Reaction #2'

$$\mathbf{s}_{2'} = \mathbf{s}_2, \quad F^{2'} = F^2 + cF^1, \quad (3.9)$$

where  $c$  is an arbitrary constant. Note that this alternative representation is exact, and that the primed reactions do not, in general, have any "physical meanings."

The conventional steady-state approximation in essence recommends that  $c$  be chosen such that the radical component of the *effective stoichiometric vector* of the primed reaction driven solely by the slower original reactions be zero. Hence for our example we would choose  $c = 2$  if  $A$  is identified as the radical (i.e.  $\mathbf{s}_{1'} = [0, -1, -2]^T$ ), while  $c = 1$  if  $B$  is so identified (i.e.  $\mathbf{s}_{2'} = [-1, 0, -1]^T$ ). In addition, the resulting differential equation for the radical is discarded and is replaced by the equation of state obtained by setting the reaction rate of the fast primed reaction to zero. For our example, this equation of state is:

$$F^{2'} = F^2 + cF^1 = 0. \quad (3.10)$$

Using this derived equation of state and the conservation of  $A + 2B - C$ , a simplified model of the original reaction system is derived, consisting of a single differential equation. As can be seen from the above derivation, the results obtained depends on the identification of the radical. In addition to the above described steady-state approximation, a different set of slightly more complicated *ad hoc* procedures are recommended for the partial-equilibrium approximation. It can be shown that each of these procedures generates a different analytical result, and the validity and accuracy of these results can only be assessed empirically.

In general, it requires experience, intuition and skill in order to make the correct derivation of the simplified models using the conventional approach.

## 4 The Basic Ideas of CSP

Consider a reaction system consisting of  $N$  unknowns (species, temperature and density) and  $R$  elementary reactions. Limiting ourselves to spatially

homogeneous problems, the governing system of ODE's can be expressed as follows:

$$\frac{dy}{dt} = \mathbf{g}(\mathbf{y}) \quad (4.1)$$

where  $\mathbf{y}$  and  $\mathbf{g}$  are  $N$ -dimensional column vectors representing the unknowns and their time rate of change, respectively. In general, the full-model  $\mathbf{g}$  can be expressed as the sum of  $R$  terms each representing a physically meaningful elementary process:

$$\mathbf{g} \equiv \sum_{r=1}^R \mathbf{s}_r F^r(\mathbf{y}) \quad (4.2)$$

where  $\mathbf{s}_r$  and  $F^r(\mathbf{y})$  are the *stoichiometric vector* and the *reaction rate* of the  $r$ -th elementary process, respectively. In general,  $N$  and  $R$  are different, and for most full-model reaction systems  $R$  is usually larger than  $N$ . Equation (4.2) is called the *physical representation* of  $\mathbf{g}$ , because each additive term can be associated with some physical meaning by the investigator.

The basic idea of CSP is to express  $\mathbf{g}$  in terms of a set of  $N$  (yet to be determined) linearly independent column basis vectors  $\mathbf{a}_i(t)$ , ( $i = 1, 2, \dots, N$ ):

$$\mathbf{g} = \sum_{i=1}^N \mathbf{a}_i f^i \quad (4.3)$$

where  $f^i$  is the "amplitude" of the  $i$ -th mode given by:

$$f^i \equiv \mathbf{b}^i \cdot \mathbf{g}, \quad i = 1, 2, \dots, N, \quad (4.4)$$

and  $\mathbf{b}^i(t)$ , ( $i=1, 2, \dots, N$ ) are *row* vectors which are orthonormal to  $\mathbf{a}_i(t)$ :

$$\mathbf{b}^i \cdot \mathbf{a}_j = \delta_{ij}, \quad i, j = 1, 2, \dots, N. \quad (4.5)$$

Obviously, the column basis vectors  $\mathbf{a}_i$ 's are some linear combinations of the physically meaningful stoichiometric vectors  $\mathbf{s}_r$ 's, and the mode amplitudes  $f^i$  are some consistent linearly combinations of the original elementary reaction rates  $F^r$ 's. The question asked by CSP is: how should the set of basis vectors  $\mathbf{a}_i$  be chosen such the "fast" modes can be neglected from (4.3) after they are exhausted?

To answer this question in general, we need to know how the mode amplitudes  $f^i$  evolve with time. Differentiating  $f^i$  with respect to time, we obtain,

with the assistance of (4.5), the following equation:

$$\frac{df^i}{dt} = \sum_{j=1}^N \Lambda_j^i f^j, \quad i = 1, 2, \dots, N, \quad (4.6)$$

where

$$\Lambda_j^i \equiv \left( \frac{db^i}{dt} + \mathbf{b}^i \cdot \mathbf{J} \right) \cdot \mathbf{a}_j, \quad i, j = 1, 2, \dots, N. \quad (4.7)$$

If the  $N \times N$  real matrix  $\Lambda_j^i$  were diagonal, the  $N$  modes would be completely decoupled; the amplitude of each mode would evolve according to its own time scale which can be identified with the reciprocal of the diagonal element. These modes can be ordered in ascending order of the magnitude of the time scales. Assuming that all modes are the decaying type, the amplitudes of the fast modes would decay toward zeros. At any moment of time, the simplified chemical kinetics model can be obtained by simply neglecting the fast modes which have become exhausted.

But in general, the matrix  $\Lambda_j^i$  is not diagonal. The mathematical theory of CSP is focussed on finding basis vectors which minimize the off-diagonal terms of this matrix. These CSP-derived basis vectors are used to compute additional CSP data which can explicitly provide physical insights about the reaction system under study.

## 5 Accomplishments

The CSP theory is developed incrementally throughout the grant period. Appendix I is a reprint of the most recently published paper<sup>[9]</sup> and contains the most complete and up-to-date summary of the theoretical developments.

We have mainly focussed on homogeneous reaction systems so that effects of diffusion are not included. A paper<sup>[10]</sup> was presented at the 1992 24th International Combustion Symposium at Sydney on the oxidation of methanol. This full model reaction system consisted of 30 chemical species plus temperature as unknowns and involved 173 reversible reactions. The CSP-derived minimum reaction system consisted only 15 species plus temperature. A copy of this published manuscript is included here as Appendix II.

A paper<sup>[11]</sup> was presented at the 1992 APS Fluid Dynamics Division Meeting dealing specifically with the effects of transverse diffusion. A full



length paper of this work is in preparation, and a copy of the unfinished manuscript is included here as Appendix III.

The CSP theory involves moderately abstract concepts in linear algebra and higher mathematics. A common comment on CSP from chemical kineticians is that the mathematics involved is too difficult. A full length paper which tries to explain CSP using simple examples and actual numbers is in preparation, and a copy of the unfinished manuscript is included here as Appendix IV.

The following is a list of the major scientific accomplishments performed under this grant:

**Computer Code CSP91** A computer code, named CSP91, was written by Dr. D. A. Goussis and contained a CSP Fortran subroutine library which can be called by reacting flow codes. This code is compatible with Chemkin<sup>[13]</sup>, and uses Chemkin database format and data files. Only minimum documentation is provided via a number of readme files. A copy of this code has been delivered to Dr. Peter Gnoffo of NASA Langley.

**Clarification of the Conventional Approaches** The reliance on experience and intuition in the conventional approaches to simplified kinetics modelling is completely removed. In essence, CSP considers the conventional approaches as **guessing** at the correct fast basis vectors. By showing that the ideal basis vectors should diagonalize  $\Lambda_j^i$ , it sets the goal for the ensuing theoretical work. It shows explicitly that the local eigen-vectors of the Jacobian of  $\mathbf{g}$  will not diagonalize  $\Lambda_j^i$ .<sup>[12]</sup>

**The Refinement Procedure Using all  $N$  Basis Vectors** The new idea of CSP is not to look for basis vectors which will precisely diagonalize  $\Lambda_j^i$ . It proposes an iteration process via a *refinement procedure*. One may begin with a reasonable guess, and the refinement procedure will generate a better iterant. The eigen-vectors of the Jacobian of  $\mathbf{g}$  is always available to provide an excellent first guess.

**The Refinement Procedure Using Only Fast Basis Vectors** In all the published papers, the refinement procedure requires that all  $N$  basis vectors participate in the algorithm even though theoretically only the fast basis vectors are of interest. In the unpublished paper presented

in Appendix IV, a simpler and much cleaner refinement procedure is introduced in which only the fast basis vectors are involved.

**The CSP-derived Equations of State** When the amplitudes of the decaying fast modes are sufficiently small in some pragmatic sense, they become equations of states. One no longer needs to apply the steady-state approximation or the partial-equilibrium approximation to derive them—such equations of state can now be computationally derived routinely.

**The CSP-derived Conservation Laws** The concept of conservation laws are generalized. In any given time epoch, reaction modes which are too slow to be included in an approximate theory can be exploited to yield locally valid conserved scalars. In other words, conservation laws can now also be computationally derived, including the familiar conservation of atomic elements.

**The Radical Pointer** Once CSP-derived basis vectors are available, a *radical pointer* can be constructed which identifies which chemical species can be algebraically solved for in terms of the others using the available equations of state. One no longer needs to guess or argue which chemical species should be eliminated from the differential equation system. The radical pointer specifically identify the “wrong” species for this purpose.

**The Fast Reaction Pointer** In general, equations of state must be used with great care. While they are doubtlessly valid approximate equations of state, they cannot be used blindly to manipulate the differential equations. For example, one may not use the  $M$  available equations of state to eliminate any  $M$  original elementary reaction rates from the original system of differential equations. Only the “fast” original elementary reaction rates can be eliminated, and wrong answers would be obtained if the wrong reactions were eliminated. The theory of CSP provides a *fast reaction pointer*, allowing the fast reactions be identified computationally.

**Minimum Reaction System** The code CSP91 written by Dr. D. A. Goussis can computationally generate from the original full-model reaction

system a minimum reaction system which contains a much smaller number of species (and includes any species of interest specifically requested by the investigator).

**Effects on Diffusion Terms** When diffusion is included in a reacting flow problem, the coupling between fast reactions and the diffusion process of the participants is strong<sup>[14]</sup>. In general, one must find the new form of the diffusion term, and in addition, one must also derived the new boudnary conditions consistent with the exhaustion of fast modes. Significant progress has been made on these issues, and the current status of this research is reported in Appendix III.

**CSP and The RNG Theory of Turbulence** While our interest in developing CSP was prompted by reacting gas flow problems, the central mathematical issue of the theory is how to deal with non-linear problems with vastly disparate time scales. The chemical kinetics problems are characterized by fast modes which are usually decaying modes, allowing the simple strategy of removing the modes when they have become negligible. In the general case, one may encounter fast modes which are highly oscillatory and lightly damped. For such "WKB" type problems, the current CSP algorithm does not work. In fact, for this type of non-linear problems, it is most likely that the system will behave stochastically in the slow time scale.

During the course of the present research, the so-called RNG theory of turbulence made its appearance in the literature. In the RNG theory, the highly oscillatory and lightly damped modes of turbulence are formally "removed" from the solution, and the collective effects of these fast modes are emulated by an eddy viscosity. Using concepts and insights gained from the CSP theory, a critique of the RNG theory<sup>[15]</sup> was published in 1992. This paper clarified some of the controversial procedures used in the RNG literature, and provided an alternative viewpoint. Most importantly, it provided an explanation for the outstanding quantitative successes of the original RNG theory.

The Grant supported graduate students Mr. David Konopka and Ms. Xin Zhu who did their master degree theses on CSP, and Mr. Andrew Tron who is currently doing his Ph.D. thesis on CSP. In addition, the Grant supported

Dr. G. A. Goussis as a research staff member who now continues his CSP research as a faculty member of the University of Patra in Greece.

Research on CSP will continue at Princeton under a AFOSR URI grant on *aerothermochemistry* which commences in 1993.

## 6 Publications and Presentations

### Refereed Publications

S. H. Lam and D.A. Goussis; "Basic Theory and Demonstration of Computational Singular Perturbation for Stiff Equations," *Modelling and Simulation of Systems*, P. Breedveld et. al. Eds., J.C. Baltzer A. G. Scientific Publishing Co., pp. 303-306, 1989.

S. H. Lam and D.A. Goussis; "Understanding Complex Chemical Kinetics with Computational Singular Perturbation," *The 22nd Symposium (International) on Combustion*, pp. 931-941, August 1988.

S. H. Lam and D. A. Goussis; "Conventional Asymptotics and Computational Singular Perturbation for Simplified Kinetics Modelling," Chapter 10 of *Lecture Notes in Physics, Reduced Kinetic Mechanisms and Asymptotics Approximations for Methane Air Flames*, M. Smooke, Ed., Springer-Verlag, 1991.

S. H. Lam and D. A. Goussis; "Sensitivity Analysis of Complex Simulations Using Basis Vectors," *Proceedings of the 13th IMACS World Congress on Computation and Applied Mathematics*, R. Vichnevetsky and J. J. H. Miller, Eds, Volume 3, p. 1992, Criterion Press, Dublin, Ireland, 1991.

S. H. Lam; "On the RNG Theory of Turbulence," *Physics of Fluids A*, **4**, 5, May 1992.

D. A. Goussis and S.H. Lam; "A Study of Homogeneous Methanol Oxidation Kinetics Using CSP," *24th Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, PA, pp. 113-120, 1992. See Appendix II.

S. H. Lam; "Using CSP to Understand Complex Chemical Kinetics," *Combustion Science and Technology*, **89**, pp. 375-404, 1993. See Appendix I.

### **Conference Presentations**

S. H. Lam, D. A. Goussis and D. Konopka; "Computational Singular Perturbation for Reacting Gasdynamics, Numerical Demonstrations I," Open Forum Session, AIAA 8th Computational Fluid Dynamics Conference, Honolulu, Hawaii, June, 1987.

S. H. Lam and D. A. Goussis; "Derivation of Simplified Multi-Step Reaction Models Using Computational Singular Perturbation," Combined Meeting of The Combustion Institute (Eastern Section) and the National Bureau of Standard's Annual Conference on Fire Research, Gaithersburg, Maryland, November 2-6, 1987.

S. H. Lam and X. Zhu; "The Split CSP Method for Reacting Flow Problems," presented at the 41st Annual Meeting of the Division of Fluid Dynamics of the American Physical Society, SUNY Buffalo, NY, November, 1988.

S. H. Lam and D. A. Goussis; "Construction of Reduced Chemical Kinetic Mechanism for a Methane Air Reaction System Using the CSP Method," presented at the Reduced Kinetic Mechanism and Asymptotic Approximations for Methane-Air Flames Workshop at UCSD, La Jolla, Ca., March, 1989.

S. H. Lam, D. A. Goussis and D. Konopka; "Time-Resolved Simplified Chemical Kinetics Modelling Using Computational Singular Perturbation," AIAA 89-0575 Aerospace Sciences Meeting, Reno, Nevada, January 9-12, 1989.

S. H. Lam and D. A. Goussis; "Reduced Chemical Kinetics for Hydrogen - Oxygen Reaction Systems," Proceedings of the 19th Spring Technical Meeting, The Combustion Institute, pp. 121-127, Dearborn Michigan, April 30-May 2, 1989.

S. H. Lam and D. A. Goussis; "On the Batched Catalytic Fluidized Beds Problem," presented at the 42nd Annual Meeting of the Division of Fluid Dynamics of the American Physical Society, NASA Ames Research Center, November, 1989.

S. H. Lam, D. A. Goussis and P. A. Gnoffo; "Reduced and Simplified Chemical Kinetics for Air Dissociation Using Computational Singular Per-

turbation," presented at the AIAA 28th Aerospace Sciences Meeting AIAA 90-0644, Reno, Nevada, January 9-12, 1990.

S. H. Lam and D. A. Goussis; "Computational Derivation of Simplified Kinetics Models," presented at the 23rd International Conference on Combustion, University of Orleans, France, July 22-27, 1990.

S. H. Lam and D. A. Goussis; "Sensitivity Analysis of Complex Chemical Systems," presented at the 1990 Reduced Kinetic Mechanism and Asymptotic Approximations for Methane-Air Flames Workshop, Cambridge, England, July, 1990.

S. H. Lam and D. A. Goussis; "Sensitivity Analysis of Complex Simulations Using Basis Vectors," presented at the 13th IMACS World Congress on Computation and Applied Mathematics, Dublin, Ireland, July 22-26, 1991. Also available as Report #1897-MAE, Princeton University, July, 1990.

S. H. Lam; "The Effects of Fast Chemical Reactions on Mass Diffusion," presented at the Annual APS Division of Fluid Dynamics Meeting at Tallahassee, Florida, November, 1992.

### **Unpublished Reports**

S. H. Lam; "Computational Singular Perturbation Procedure for Stiff Equations," Mechanical and Aerospace Engineering Report No. 1697-MAE, Princeton University, 1985.

S. H. Lam; "On Steady-State and Partial Equilibrium Approximations for Chain Reactions," Mechanical and Aerospace Engineering Report No. 1722-MAE, Princeton University, 1985.

S. H. Lam and D. A. Goussis; "Research on Computational Singular Perturbation (Progress Report #1: Basic Theory," Mechanical and Aerospace Engineering Report No. 1779(a)-MAE, Princeton University, 1987.

S. H. Lam and D. A. Goussis; "Research on Computational Singular Perturbation (Progress Report #2: Numerical Demonstrations)," Mechanical and Aerospace Engineering Report No. 1779(b)-MAE, Princeton University, 1987.

S. H. Lam and D. A. Goussis; "Understanding Complex Chemical Kinetics with Computational Singular Perturbation," Mechanical and Aerospace Engineering Report No. 1799-MAE, Princeton University, 1988.

S. H. Lam and D. A. Goussis; "Recent Developments in Simplified Kinetics Modelling for Large Reaction Systems," Princeton University Report #1864-MAE, 1989.

### Work in Progress

S. H. Lam; "On Reacting Flows with Diffusion and Fast Chemical Reactions," MAE Report #1999, 1992. See Appendix III.

S. H. Lam and D. A. Goussis; "The CSP Method for Simplifying Kinetics," MAE Report #1946, 1992. See Appendix IV.

## 7 Epilogue

With the support of this NASA Grant, we have been able to establish a firm mathematical foundation for CSP. The "correctness" of the results is beyond dispute—the numerical solutions of the full-model and the CSP-derived simplified model are guaranteed to stay below a user-specified threshold theoretically, and confirmed by the computer code CSP91. The idea that computational power can be exploited to yield physical insights is new and will surely become more important in the future.

## References

- [1] Aiken, R. C., *Stiff Computation*, Oxford University Press, 1985.
- [2] Lam, S. H., "Singular perturbation for stiff equations using numerical methods", in *Recent Advances in the Aerospace Sciences*, Corrado Casci, Ed., Plenum Press, New York and London, pp.3-20, 1985.
- [3] Williams, F.A., *Combustion Theory, The fundamental theory of chemically reacting systems*, 2nd edition, Benjamin/Cummings Publ. Co., Menlo Park, Ca., 1985.
- [4] Benson, S. W., "The induction period in chain reactions," *J. Chem. Phys.* **20** p.1605, 1952.
- [5] Bowen, J. R., Acrivos, A. and Oppenheim, A. K., "Singular perturbation refinement to quasi-steady state Approximation in chemical kinetics," *Chem. Eng. Sci.* **18**, p.177, 1963.

- [6] Peters, N., "Numerical simulation of combustion phenomena," Glowinski, R., Larrourou, B and Temem, R., Eds., *Lecture Notes in Physics* 241, p. 90-109, Springer-Verlag, New York, 1985.
- [7] Peters, N., "Systematic Reduction of Flame Kinetics," in *Fluid Dynamical Aspects of Combustion Theory*, M. Onofri and A. Tesei, Eds., *Pitman Research Notes in Mathematics Series*, Longman Scientific and Technical, Longman House, Burnt Mill, Harlow, Essex, UK, 1991. (Also published by John Wiley in the U.S.).
- [8] Frenklach, M.; "Reduction of Chemical Reaction Models," *Numerical Approaches to Combustion Modeling*, Oran and Boris, Eds., *AIAA Progress in Astronautics and Aeronautics*, **135**, 1991.
- [9] Lam, S. H.; "Using CSP to Understand Complex Chemical Kinetics," *Combustion Sci. and Tech.*, **89**, pp. 375-404, 1993.
- [10] Goussis, D. A. and Lam, S. H., "A study of homogeneous methanol oxidation kinetics using CSP," *Proceedings of the 24th International Symposium on Combustion*, University of Sydney, Sydney, Australia, July 5-10, 1992.
- [11] Lam, S. H.; "The Effects of Fast Chemical Reactions on Mass Diffusion," presented at the Annual APS Division of Fluid Dynamics Meeting at Tallahassee, Florida, November, 1992.
- [12] Maas, U. and Pope, S. B., "Simplifying Chemical Kinetics: Intrinsic Low-Dimensional Manifolds in Composition Space," *Combust. Flame*, **88**, pp. 239-264, 1992.
- [13] Kee, R. J., Rupley, F. M. and Miller, J. A., Sandia Report SAND89-8009, 1989.
- [14] Goddard, J. D., "Consequences of the Partial-equilibrium Approximation for Chemical Reaction and Transport," *Proc. R. Soc.* **431** pp.271-284, 1990.
- [15] Lam, S. H.; "On the RNG Theory of Turbulence," *Physics of Fluids A*, **4**, 5, May, 1992.



## Appendix I

### Using CSP to Understand Complex Chemical Kinetics

*Combustion Science and Technology*, **86**, pp. 375-404, 1993

# Using CSP to Understand Complex Chemical Kinetics\*

S. H. Lam

Department of Mechanical and Aerospace Engineering  
School of Engineering and Applied Science  
Princeton University  
Princeton, NJ 08544

## Abstract

The conventional methods of simplified kinetics modeling through the use of partial-equilibrium and quasi-steady approximations are reviewed and critiqued. The method of *computational singular perturbation* (CSP) is then presented with special emphasis on the interpretation of CSP data to obtain physical insights on massively complex reaction systems. A simple example is used to demonstrate how CSP deals with complex chemical kinetics problems without the benefits of intuition and experience.

## 1 Introduction

An ideal scenario in the (near) future for the study of chemical kinetics would be that a comprehensive, reliable and up-to-date database of validated reaction rates is readily available to any researcher interested in any reasonable reaction system of interest. Using a suitable stiff solver, one can routinely compute for the numerical solution of a massively complex chemical kinetics system. However, the extraction of *physical insights* about the

---

\*This work is supported by NASA Langley's Aerothermodynamics Branch, Space Systems Division.

reaction system from the massive printouts is a different matter, and remains a formidable task. Generally speaking, answers to the following questions are highly valued:

1. How can a *reduced reaction system*, involving a much smaller set of chemical species and elementary reactions, be derived which can approximate the original massive reaction system both qualitatively and quantitatively?
2. How can the rate-controlling elementary reactions be identified? What rate constants must be known accurately? What rate constants need not be known accurately provided that they are “sufficiently large”?
3. Which elementary reactions can be considered fast reactions in the time interval of interest so that appropriate approximations can be applied to obtain useful approximate algebraic relations between the species?
4. Which chemical species can be considered as “intermediaries” or “radicals?” in the time interval of interest so that their concentrations can be obtained from these approximate algebraic relations?

In the present paper, we shall call approximate algebraic relations between the species “*equations of state*.” In addition, we shall use the word “radical” to connote a special meaning in the CSP context instead of its normal chemical structure context. An operational definition for a CSP radical based on its mathematical role in the CSP theory will be given later. In most cases, a CSP radical will be found to be a chemical radical, and *vice versa*, but not always. To avoid confusion, we shall not use the term “intermediaries” altogether.

Item #1 is important pragmatically because computational cost is a strong function of the number of chemical species. Questions in item #2 needs no justification; one can claim insights on the reaction system only if these questions can be satisfactorily answered. The conventional methodology deals with items #3 and #4 first, mainly by *guessing* based on experience and intuition. Some talented investigators simply know which reactions are fast and which chemical species are radicals under what conditions for certain reaction systems (Peters, 1985, 1991; Peters and Williams, 1987; Chelliah and Williams, 1990; Bilger *et. al.* 1990, 1991). For the less gifted, data from

numerical solutions of the full kinetics equations can be used to provide hints in the identifications. Once the fast reactions and the radicals are correctly identified, standard techniques are available to obtain answers to questions in items #1 and #2.

The method of *computational singular perturbation* (CSP) (Lam, 1985; Lam *et. al.*, 1988a, 1988b, 1989, 1991a, 1991b; Goussis *et. al.*, 1990, 1992) provides a programmable mathematical algorithm to proceed routinely without the benefits of experience and intuition. It can be used to verify the validity of simplified models derived by *ad hoc* methods, and it can be used to deal with massively complex problems beyond the reach of such methods. Physical understanding of the reaction system under investigation can easily be extracted from the CSP data generated.

## 2 Statement of the Problem

Consider a reaction system of  $N$  unknowns<sup>1</sup> denoted by the column *state vector*  $\mathbf{y} = [y^1, y^2, \dots, y^N]^T$ . The governing system of ODE is:

$$\frac{d\mathbf{y}}{dt} = \mathbf{g}(\mathbf{y}) \quad (1)$$

where

$$\mathbf{g}(\mathbf{y}) \equiv \sum_{r=1}^R \mathbf{s}_r F^r(\mathbf{y}), \quad (2)$$

$R$  is the number of elementary reactions being included in the reaction system,  $\mathbf{s}_r$  and  $F^r(\mathbf{y})$  are the *stoichiometric vector* and the *reaction rate* of the  $r$ -th elementary reactions, respectively. The  $N$ -dimensional column vector  $\mathbf{g}$  is the overall reaction rate vector, and can be interpreted as the “velocity vector” of  $\mathbf{y}$  in the  $N$ -dimensional  $y$ -space. For a massively complex problem,  $N$  and  $R$  can be large numbers, and the accuracy or reliability of the available rate constants is usually less than ideal. Assuming that adequate computing power is available, the computation of the numerical solution of (1) is not an issue. The challenge is to obtain answers to questions in items #1 and #2 in §1.

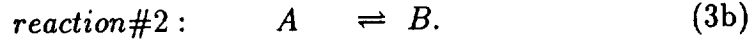
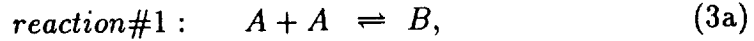
---

<sup>1</sup>The  $N$ -dimensional column vector may include temperature, total density, etc. in addition to chemical species

As previously indicated, the conventional method relies completely on the skill of the investigator to identify the fast reactions and the radicals. Once the identifications are made, the subsequent theoretical development proceeds relatively routinely. The interested reader is referred to Appendix B of Williams (1985) for a detailed exposition of the conventional methodology.

## 2.1 The Conventional Methodology by Example

We shall use a simple hypothetical reaction system to demonstrate the conventional methodology. Let the state vector be  $\mathbf{y} = [A, B, C]^T$  where  $A$  and  $B$  are chemical concentrations and  $C$  is temperature. The reaction system consists of two elementary reactions:



The stoichiometric vectors and the reaction rates are:

$$\mathbf{s}_1 = [-2, 1, \Delta H_1]^T, \quad F^1 = k_1(A^2 - K_1B), \quad (4a)$$

$$\mathbf{s}_2 = [-1, 1, \Delta H_2]^T, \quad F^2 = k_2(A - K_2B). \quad (4b)$$

where the reaction rate coefficients  $k_1, k_2$  and the equilibrium constants  $K_1, K_2$  are known and for the sake of simplicity their dependence on  $C$  is assumed negligible. The heat of reaction (in the proper unit) for the two reactions are denoted by  $\Delta H_1$  and  $\Delta H_2$ , respectively.

The system of ODE is:

$$\frac{d\mathbf{y}}{dt} = \mathbf{s}_1 F^1 + \mathbf{s}_2 F^2 \quad (5)$$

which can be written out as follows:

$$\frac{dA}{dt} = -2F^1 - F^2, \quad (6a)$$

$$\frac{dB}{dt} = F^1 + F^2, \quad (6b)$$

$$\frac{dC}{dt} = \Delta H_1 F^1 + \Delta H_2 F^2. \quad (6c)$$

The initial conditions,  $A(0)$ ,  $B(0)$  and  $C(0)$ , are given. It can easily be shown that as  $t \rightarrow \infty$ ,  $A \rightarrow K_1/K_2$  and  $B \rightarrow K_1/K_2^2$ . Normalizing the unknowns intelligently, we have  $y_* = [A_*, B_*, C_*]^T$ :

$$A_* = AK_2/K_1, \quad (7a)$$

$$B_* = BK_2^2/K_1, \quad (7b)$$

$$C_* = CK_2/(\Delta H_2 K_1). \quad (7c)$$

The system of ODE for  $A_*$ ,  $B_*$  and  $C_*$  is:

$$\frac{dA_*}{dt} = -\frac{2}{K_2} K_1 k_1 (A_*^2 - B_*) - k_2 (A_* - B_*), \quad (8a)$$

$$\frac{dB_*}{dt} = K_1 k_1 (A_*^2 - B_*) + K_2 k_2 (A_* - B_*), \quad (8b)$$

$$\frac{dC_*}{dt} = \frac{\Delta H_1}{K_2 \Delta H_2} K_1 k_1 (A_*^2 - B_*) + k_2 (A_* - B_*). \quad (8c)$$

The initial conditions are:

$$A_*(0) = A(0)K_2/K_1, \quad (9a)$$

$$B_*(0) = B(0)K_2^2/K_1, \quad (9b)$$

$$C_*(0) = C(0)K_2/(\Delta H_2 K_1). \quad (9c)$$

As  $t \rightarrow \infty$ , we have  $A_* \rightarrow 1$  and  $B_* \rightarrow 1$ .

Because this reaction system is a hypothetical one, the concept of conservation of atomic species cannot be applied—we do not know what atomic species are involved. However, it can easily be verified mathematically that:

$$(\Delta H_1 - \Delta H_2)A + (\Delta H_1 - 2\Delta H_2)B + C = \text{Constant} \quad (10)$$

is an exact “integral of motion” valid for all time, and can be physically interpreted as a statement of conservation of total energy.

For this simple example, if the “speeds” of the two reactions are competitive, there is no simplification available and little or no general statement can be made. However, when one reaction is much faster—in some sense—than the other, then certain mathematical simplifications are available and certain useful general statements can be made. Intuitively, we expect a rapid transient period in which the fast reaction would *dominate*, followed by a slower

evolutionary period in which the slow reaction would be *controlling*. In general, we expect to be able to neglect some of the slower reactions in the rapid transient period. However, it is well known that the handling of the nearly exhausted fast reactions in the slow evolutionary period requires considerable care—it suffices to say here that they cannot be summarily neglected.

## 2.2 The Case of reaction #1 being faster ( $\frac{K_2 k_2}{K_1 k_1} \ll 1$ )

In the rapid transient period, the fast reaction #1 dominates. Hence, the slow reaction #2 can be neglected to yield the simplified model:

$$\frac{dA_*}{dt} \approx -\frac{2}{K_2} K_1 k_1 (A_*^2 - B_*), \quad (11a)$$

$$\frac{dB_*}{dt} \approx K_1 k_1 (A_*^2 - B_*), \quad (11b)$$

$$\frac{dC_*}{dt} \approx \frac{\Delta H_1}{K_2 \Delta H_2} K_1 k_1 (A_*^2 - B_*). \quad (11c)$$

with (9a), (9b) and (9c) serving as the initial conditions. It is easy to show that in addition to (10), the following

$$K_2 A_* + 2B_* \approx \frac{K_2^2}{K_1} (A(0) + 2B(0)) \quad (12)$$

is approximately “conserved” (remains constant) during this period.

At the end of this period, the fast reaction #1 will have become “exhausted,” and  $A_*$  and  $B_*$  will be approximately related by  $B_* \approx A_*^2$ . In the slow evolutionary period which follows, an approximate equation of state is obtained by setting  $F^1$  to zero. This is called the *partial-equilibrium* approximation and a special follow-up procedure is recommended. First, one of the participants of reaction #1 is somehow declared a radical. If  $B_*$  is so declared, (8b) is used to eliminate the contribution from reaction #1 (i.e.  $K_1 k_1 (A_*^2 - B_*)$ ) from the rest of the equations. Then, the approximate equation of state is differentiated with respect to time and used to eliminate  $dB_*/dt$ . The following simplified model is obtained:

$$B_* \approx A_*^2, \quad (13a)$$

$$\frac{dA_*}{dt} \approx \frac{K_2 k_2}{K_2 + 4A_*} (A_* - B_*), \quad (13b)$$

$$\frac{dC_*}{dt} \approx [1 - \frac{\Delta H_1}{\Delta H_2} (\frac{K_2 + 2A_*}{K_2 + 4A_*})] k_2 (A_* - B_*). \quad (13c)$$

It can easily be verified that the same answer is obtained (in contrast to results in §2.3.2 later) if  $A_*$  is chosen as a radical. It is important to note that (13b) and (13c) are *not* obtained by substituting (13a) into (8a) and (8c). In fact, (13a) must *never* be used in (8a), (8b) or (8c). The initial conditions can be found from  $B_* \approx A_*^2$  and (12):

$$A_*(0+) \approx \frac{K_2}{4} \left[ \sqrt{1 + \frac{8(A(0) + 2B(0))}{K_1}} - 1 \right] \quad (14)$$

with  $B_*(0+)$  and  $C_*(0+)$  given by (13a) and (10). Note that  $k_1$  does not appear at all in (13a), (13b) or (13c), hence its value must be unimportant provided that it is "sufficiently large." In this time period, (13a), (13b) and (13c) together behave as a "one-step" reaction with an *effective stoichiometric vector* and an *effective reaction rate*, and generate approximate solutions which satisfy (10) exactly.

### 2.3 The Case of reaction #2 being faster ( $\frac{K_1 k_1}{K_2 k_2} \ll 1$ )

In the rapid transient period, reaction #1 is neglected to yield the simplified model:

$$\frac{dA_*}{dt} \approx -k_2 (A_* - B_*), \quad (15a)$$

$$\frac{dB_*}{dt} \approx K_2 k_2 (A_* - B_*), \quad (15b)$$

$$\frac{dC_*}{dt} \approx k_2 (A_* - B_*). \quad (15c)$$

again with (9a), (9b) and (9c) serving as the initial conditions. It is easy to show that

$$K_2 A_* + B_* \approx \frac{K_2^2}{K_1} (A(0) + B(0)) \quad (16)$$

is approximately conserved (remains constant) during this period.

At the end of this period,  $A_*$  and  $B_*$  will be approximately related by  $B_* \approx A_*$ . For this case, we shall present both the partial-equilibrium approximation and the quasi-steady approximation in the slow evolutionary period. We shall see that they produce different answers.



### 2.3.1 The Partial-Equilibrium Approximation

In the slow evolutionary period, we can proceed as before by assuming elementary reaction #2 to be in partial-equilibrium. Using the same recommended procedure, we obtain the following simplified model:

$$B_* \approx A_*, \quad (17a)$$

$$\frac{dA_*}{dt} \approx \frac{K_1 k_1}{1 + K_2} (B_* - A_*^2), \quad (17b)$$

$$\frac{dC_*}{dt} \approx \left[ \frac{K_2 + 2}{K_2 + 1} - \frac{\Delta H_1}{\Delta H_2} \right] \frac{K_1 k_1}{K_2} (B_* - A_*^2). \quad (17c)$$

with initial conditions:

$$A_*(0+) \approx \frac{K_2^2(A(0) + B(0))}{K_1(1 + K_2)} \quad (18)$$

with  $B_*(0+)$  and  $C_*(0+)$  given by (17a) and (10). It is emphasized again that (17b) and (17c) are *not* obtained by substituting (17a) into (8b) and (8c). It can be shown that the partial-equilibrium approximation above can be formally justified when  $K_1 k_1 \ll K_2 k_2$  and  $A_*(0) = O(1)$ , with no restriction on the magnitude of  $K_2$ , and the resulting approximate solutions satisfy (10) exactly.

### 2.3.2 The Quasi-Steady Approximation

Alternatively, we can declare either the species  $B_*$  or  $A_*$  to be a radical in this period. The *quasi-steady approximation* neglects the time derivative term from the ODE of the radical to yield an approximate equation of state. If  $B_*$  is so declared, the approximate equation of state obtained from (8b) is used to simplify (8a) and (8c). The resulting set of equations (without (8b)) is then augmented by the approximate equation of state to yield the simplified model. We obtain:

$$B_* \approx A_*, \quad (19a)$$

$$\frac{dA_*}{dt} \approx \frac{K_1 k_1}{K_2} (B_* - A_*^2), \quad (19b)$$

$$\frac{dC_*}{dt} \approx \left[ 1 - \frac{\Delta H_1}{\Delta H_2} \right] \frac{K_1 k_1}{K_2} (B_* - A_*^2). \quad (19c)$$

with initial condition (18). Note that (19b) and (19c) agree with (17b) and (17c) and satisfy (10) *only* when  $K_2 \gg 1$ . If  $K_2 \ll 1$ , then  $A_*$  should have been declared a radical instead, and a different result valid only in this limit is obtained. If  $K_2$  is of  $O(1)$ , then the quasi-steady approximation is simply incorrect—while the partial-equilibrium approximation is valid for all  $K_2$ .

Again, the value of  $k_2$  does not appear in the simplified model in the slow evolutionary period. The inference is that its value is unimportant provided that it is sufficiently large.

## 2.4 Comments on Conventional Asymptotics

The above example prompts the following questions and observations:

1. Exact algebraic “conservation laws” such as conservation of atomic species and conservation of energy frequently exist in chemical kinetics problems. In the above example, (10) is such a conservation law. Can such conservation laws, when they exist, be mathematically identified and derived?
2. In the rapid transient period, additional temporary approximate conservation laws may exist. In the above example, (12) and (16) are temporary approximate conservation laws valid for the respective cases. Can such temporary approximate conservation laws, when they exist, also be mathematically derived?
3. When a fast reaction exhausts itself, its net reaction rate is *not* negligible in general from the governing equations. For example, when reaction #1 is the faster reaction, the exhausted  $F^1$  is not zero in the slow evolutionary period but is, to “leading order,” given by:

$$K_1 k_1 (A_*^2 - B_*) \rightarrow -\frac{(K_2 + 2A_*)}{(K_2 + 4A_*)} K_2 k_2 (A_* - B_*), \quad (20a)$$

or

$$F^1 \rightarrow -\frac{K_1 + 2A}{K_1 + 4A} F^2, \quad (20b)$$

which can be derived by comparing (8a) with (13b). In other words, when a fast elementary reaction is exhausted, its *net* reaction rate may be competitive with the slower reactions.

4. In any slow evolutionary period, the temporary approximate conservation laws valid in the previous periods are replaced by approximate equations of state obtained by applying the partial-equilibrium or the quasi-steady approximation. In our example, (13a), (17a) and (19a) are such equations of state for the respective cases. Can these equations of state be mathematically derived? How is (13a) related to (20b)?
5. In a slow evolutionary period, the values of the exhausted fast reaction rate constants are not important provided that they are fast enough. In our example, the fastest rate coefficient (either  $k_1$  or  $k_2$ ) does not appear in the simplified models when  $M = 1$ . From the computation point of view, their absence means the simplified model is no longer “stiff” (Aiken, 1985).
6. To get started on the conventional method, one must somehow decide that certain reactions are faster than others based on some vague, intuitive judgment. Unlike linear problems, the “speed” of a “reaction mode” in a non-linear problem can depend strongly on the state of the system. For example, even if  $K_2 k_2 \gg K_1 k_1$ , reaction #1 can still dominate reaction #2 initially provided that  $A_*(0)$  is sufficiently large. Since we are clearly interested in non-linear problems, a mathematical criterion for the identification of fast reactions is very much needed.
7. Even after the fast reactions have somehow been identified, there is still the question on whether the partial-equilibrium or the quasi-steady approximation should be used to generate the approximate equations of state, and which species—radicals—can be eliminated by using these algebraic equations.
8. In Williams’ book (1985), a radical is described as a chemical species which is “neither initial reactants nor principal products,” a description too vague to be useful. In §2.3, we saw that whether  $A_*$  or  $B_*$  could justifiably be declared a radical depends on the magnitude of  $K_2$ , and that when  $K_2 = O(1)$  the quasi-steady approximation is simply wrong.
9. We shall adopt a pragmatic but precise definition for a radical in the CSP context: *a chemical species is a CSP-radical if its ODE can be replaced by an approximate equation of state.* For the moment, we

shall leave the questions of how to identify the radical(s) and how to solve for them from CSP-derived equations of state until the concepts of “radical pointer” and “radical correction” are introduced later.

10. We emphasize here again that the approximate equations of state obtained from the partial-equilibrium approximation must *never* be used directly in the original governing equations—the so-called recommended procedure must be followed. However, the approximate equations of state obtained from the quasi-steady approximation may be used more freely, but the validity of the results is more restricted. In fact, the quasi-steady approximation can be viewed as an additional *ad hoc* restriction imposed on the results of an appropriately applied partial-equilibrium approximation.
11. Conventional asymptotics assumes that the investigator is not only capable of non-dimensionalizing the variables intelligently, but also competent to take advantage of the presence of large or small parameter(s) in the resulting formulation. Can a theoretical structure be developed such that intelligent non-dimensionalization is not required?
12. In general, the conventional “magnitude” of a dimensional vector  $\mathbf{y}$  computed using the standard inner product may not make physical sense. In the above example,  $\|\mathbf{y}\|_2 = (A^2 + B^2 + C^2)^{1/2}$  makes no physical sense at all. In the language of mathematics, the “norm” of the vector space of  $\mathbf{y}$  needs to be defined. Hence if intelligent non-dimensionalization is not assumed, the concept of a “good approximation” needs to be explicitly clarified.

### 3 The Goal and the Idea of CSP

The conventional method is only viable for relatively simple problems for which adequate amount of experience and intuition have been accumulated, and that the algebra involved is manageable. For massively complex problems with large values of  $N$  and  $R$ , a better method is clearly needed.

### 3.1 The Goal

The goal of CSP is to computationally derive time-resolved simplified models for massively complex chemical systems assuming that the appropriate reaction rate database is available. The *novel* feature of CSP is that the power of the modern computer is exploited not only to construct the numerical solutions, but also *to derive the approximate equations*.

The output of CSP is a set of numbers called the CSP data. An essential attribute of CSP data is that it must be easy to interpret. Answers to questions such as:

- how many approximate equations of state are available and how can they be derived?
- which species can be considered radicals—in the CSP context—so that they can be computed from these equations of state?
- which elementary reactions are controlling the reaction rate of the system? and
- what is the minimum reduced reaction system that will generate an approximate solution with a user-specified accuracy?

and others will be provided by the CSP data.

### 3.2 The Idea

The physical problem is completely specified by  $\mathbf{g}(\mathbf{y})$ , a non-linear function of  $\mathbf{y}$  obtained by summing all the physical processes which contribute to the time rate of change of  $\mathbf{y}$ . The question is: is there a better representation than the physical representation?

A representation is said to be a *physical representation* when the theoretician formulating the problem can explain and interpret each term physically. Equation (2) is such a representation because as written each term represents the contribution of each of the  $R$  reactions included in the full model. Must we always write  $\mathbf{g}$  in this particular form? Since  $\mathbf{g}$  is a  $N$ -dimensional vector, it can always be expressed in terms of a set of arbitrarily chosen  $N$  linearly

independent column *basis vectors*,  $\mathbf{a}_i$ ,  $i = 1, 2, \dots, N$ . When some other set of basis vectors is used,  $\mathbf{g}$  has an *alternative representation*:

$$\mathbf{g} = \sum_{i=1}^N \mathbf{a}_i f^i \quad (21)$$

where  $f^i$ , called the *amplitude* of the  $i$ -th *mode*, is given by:

$$f^i(\mathbf{y}) \equiv \mathbf{b}^i \odot \mathbf{g} = \sum_{r=1}^R B_r^i F^r, \quad i = 1, 2, \dots, N, \quad (22)$$

where

$$B_r^i \equiv \mathbf{b}^i \odot \mathbf{s}_r, \quad i = 1, 2, \dots, N, \quad r = 1, 2, \dots, R, \quad (23)$$

and  $\odot$  is the dot product operator of the  $N$ -dimensional vector space. When properly normalized,  $f^i$  can also be considered as a “progress variable” for the  $i$ -th mode. The set of  $N$  row vectors  $\mathbf{b}^i$  are the inverses of  $\mathbf{a}_i$ ; together they satisfy the following orthonormal condition:

$$\mathbf{b}^i \odot \mathbf{a}_j = \delta_j^i, \quad i, j = 1, 2, \dots, N. \quad (24)$$

Note that once the set  $\mathbf{a}_i$  is chosen, the associated set  $\mathbf{b}^i$  is straightforwardly computed. Note also that  $B_r^i$  is not necessarily dimensionless unless deliberately made so.

In our example, we have  $N = 3$ . The physical representation chooses (by default) the following column basis vectors:

$$\mathbf{a}_1 = \mathbf{s}_1, \quad (25a)$$

$$\mathbf{a}_2 = \mathbf{s}_2, \quad (25b)$$

$$\mathbf{a}_3 = \mathbf{s}_3 = [0, \quad 0, \quad 1]^T. \quad (25c)$$

where we have added  $\mathbf{s}_3$  to form a complete set. Any vector which is linearly independent of  $\mathbf{a}_1$  and  $\mathbf{a}_2$  may also be used. The associated row basis vectors are obtained by solving (24):

$$\mathbf{b}^1 = [-1, \quad -1, \quad 0], \quad (26a)$$

$$\mathbf{b}^2 = [1, \quad 2, \quad 0], \quad (26b)$$

$$\mathbf{b}^3 = [\Delta H_1 - \Delta H_2, \quad \Delta H_1 - 2\Delta H_2, \quad 1]. \quad (26c)$$

We can readily verify that:

$$f^1 = \mathbf{b}^1 \odot \mathbf{g} = F^1. \quad (27a)$$

$$f^2 = \mathbf{b}^2 \odot \mathbf{g} = F^2. \quad (27b)$$

$$f^3 = \mathbf{b}^3 \odot \mathbf{g} = F^3 = 0. \quad (27c)$$

The CSP idea is very simple: instead of using the physically meaningful stoichiometric vectors as the default basis vectors, let's exploit the theoreticians' prerogative of trying different alternatives—may be something else works better.

### 3.3 Same Problem, Different Basis Vectors

We shall rework the first case of our example using dimensional formulation.

Instead of the physically meaningful stoichiometric vectors, we shall use, *without comments at this point*, the following set of basis vectors:

$$\mathbf{a}_1 = [-2, \quad 1, \quad \Delta H_1]^T = \mathbf{s}_1, \quad (28a)$$

$$\mathbf{a}_2 = \frac{1}{K_1 + 4A} [K_1, 2A, (K_1 + 4A)\Delta H_2 - (K_1 + 2A)\Delta H_1]^T, \quad (28b)$$

$$\mathbf{a}_3 = [0, \quad 0, \quad 1]^T. \quad (28c)$$

The following row vectors are their inverses and together they satisfy (24):

$$\mathbf{b}^1 = \frac{1}{K_1 + 4A} [-2A, \quad K_1, \quad 0], \quad (29a)$$

$$\mathbf{b}^2 = [1, \quad 2, \quad 0], \quad (29b)$$

$$\mathbf{b}^3 = [\Delta H_1 - \Delta H_2, \quad \Delta H_1 - 2\Delta H_2, \quad 1]. \quad (29c)$$

The amplitudes of the modes are:

$$f^1 = \mathbf{b}^1 \odot \mathbf{g} = F^1 + \frac{K_1 + 2A}{K_1 + 4A} F^2, \quad (30a)$$

$$f^2 = \mathbf{b}^2 \odot \mathbf{g} = F^2, \quad (30b)$$

$$f^3 = \mathbf{b}^3 \odot \mathbf{g} = F^3 = 0. \quad (30c)$$

In terms of these basis vectors, the original reaction system becomes:

$$\frac{dy}{dt} = \mathbf{a}_1 f^1 + \mathbf{a}_2 f^2 + \mathbf{a}_3 f^3 \quad (31)$$

We can rewrite (31) in long-hand notation as follows:<sup>2</sup>

$$\frac{dA}{dt} = -2f^1 + \frac{K_1}{K_1 + 4A}f^2, \quad (32a)$$

$$\frac{dB}{dt} = f^1 + \frac{2A}{K_1 + 4A}f^2, \quad (32b)$$

$$\frac{dC}{dt} = [\Delta H_1]f^1 + [\Delta H_2 - (\frac{K_1 + 2A}{K_1 + 4A})\Delta H_1]f^2. \quad (32c)$$

Taking the inner product of  $\mathbf{b}^i$  with (31), we obtain:

$$\frac{1}{K_1 + 4A} \frac{d}{dt} [-A^2 + K_1 B] = f^1, \quad (33a)$$

$$\frac{d}{dt} [A + 2B] = f^2, \quad (33b)$$

$$\frac{d}{dt} [(\Delta H_1 - \Delta H_2)A + (\Delta H_1 - 2\Delta H_2)B + C] = f^3. \quad (33c)$$

We shall assume for the moment that somehow the modes have been ordered in descending speed—mode #1 is faster than mode #2. This is physically equivalent to saying that  $F^1$  is estimated to be faster than  $F^2$ . Reaction rate  $f^3$  of mode #3 is, for this problem, identically zero.

### 3.3.1 Exact Conservation Law

Whenever the amplitude of a slow mode is considered “negligible,” it can be summarily neglected. Since for this problem  $f^3 = 0$ , mode #3 is always negligible, (33c) recovers (10), the conservation law for energy obtained earlier. However, a dormant mode does not always yield a conservation law. See §7.2 later.

### 3.3.2 The Rapid Transient Period

In the rapid transient period, we assume that the dominant mode is  $f^1$ , while  $f^2$  and  $f^3$  are negligible in comparison.<sup>3</sup> The simplified model is:

$$\frac{dy}{dt} \approx \mathbf{a}_1 f^1. \quad (34)$$

<sup>2</sup>Compare them with (6a), (6b) and (6c).

<sup>3</sup>A slower mode may not necessarily be negligible in this period; if it is not, it *must* be kept.



Neglecting the right-hand side of (33b) and (33c), we recover (12) and (10), the temporary and permanent conservation laws obtained earlier. The solution of (34) automatically satisfies these constraints. As time progresses, mode #1 decays rapidly and becomes exhausted as  $f^1 \rightarrow 0$ , and  $y$  approaches a fixed point.

### 3.3.3 The Slow Evolutionary Period

In the slow evolutionary period, (12) ceases to be valid, but the exhausted mode #1 replaces it with a new approximate equation of state:

$$f^1(y) = \sum_{r=1}^R B_r^1 F^r(y) \approx 0, \quad (35a)$$

$$= F^1 + \frac{K_1 + 2A}{K_1 + 4A} F^2 \approx 0, \quad (35b)$$

which is the counterpart of (13a), and agrees with it in the  $|F^1| \gg |F^2|$  limit. However, unlike (13a), which we emphasized must never be substituted directly into the original governing equations, (35a) needs no such admonition and can be so used freely. Using it in (31), we obtain the simplified model for this period:

$$\frac{dy}{dt} \approx a_2 f^2. \quad (36)$$

Solution of (36) automatically satisfies (35a) if it is satisfied initially. No decision on which species should be eliminated (*i.e.* considered as a radical) was needed so far. All results obtained can be shown to be consistent with the conventional method in the asymptotic limit of reaction #1 being much faster than reaction #2.

### 3.3.4 Response to a Slow Third Reaction

For our simple example with only two reactions and three unknowns, the reaction system reaches its steady state after both modes #1 and #2 are exhausted. What happens if there is a third reaction? Denote the stoichiometric vector and reaction rate of the third reaction by  $s_3$  and  $F^3$  respectively. In addition, assume that the three stoichiometric vectors are linearly independent, and that  $|F^1| \gg |F^2| \gg |F^3|$  so that the added reaction is the slowest.

Using the same basis vectors in §3.3, we can proceed as before. The main impact of this complication is that  $f^i = \mathbf{b}^i \odot \mathbf{g}$  now contain contribution from  $F^3$ . After mode #2 is exhausted, a even slower mode #3 will take over. One can easily verify that the simplified model for this period is:

$$\frac{dy}{dt} \approx a_3 f^3. \quad (37)$$

Note that in this time period, the response of  $A$  and  $B$  to the slow third reaction is negligible; only  $C$  responds significantly.

### 3.4 The Obvious Questions

It can be shown that the three simplified models (34), (36) and (37) displayed above are the leading-order approximations in the asymptotic limit of  $|F^1| \gg |F^2| \gg |F^3|$  for the indicated time periods, as obtained earlier in §2.2. Hence, the alternative representation of  $\mathbf{g}$  using the special set of basis vectors ((28a), (28b) and (28c)) is clearly a good idea in this limit.

It can easily be verified that (28a), (28b) and (28c) are the right eigenvectors of the Jacobian of  $\mathbf{g}$  in the limit of  $k_1 K_1 \gg k_2 K_2$ . Why do these special basis vectors allows us to summarily neglect the exhausted fast modes, while the same casualness would not be tolerated previously? What is the relationship between the conventional methods and the eigen-vectors of the Jacobian? How does one know that the basis vectors which worked well for one set of initial conditions will work for a different set of initial conditions? What happens when  $k_2 K_2 / k_1 K_1$  is only moderately small?

Additional questions are: How does one extract physically interesting information from these basis vectors? Which species can be considered a radical? How can the accuracy of these models be improved? How can the whole procedure be generalized to deal with a massively complex problem?

## 4 The Ideal Basis Vectors

Given any set of  $N$  linearly independent basis vectors, one can always decompose the  $N$ -dimensional vector  $\mathbf{g}$  into  $N$  additive components or modes. Most investigators use the physically meaningful stoichiometric vectors as basis vectors by default. When the set used is non-ideal, the speed ranking

of the modes is unclear, and the residual net reaction rate of an exhausted fast reaction mode can not be neglected in general, and must be treated with great care. We have seen in the above example that the use of an intelligently chosen alternative set of basis vectors can make a difference. A good set of basis vectors not only should order the modes according to their speed, but also guarantee that the residual net reaction rate of an exhausted mode be negligible.

To find out how the amplitude of each mode evolves with time, we differentiate (1) with respect to time to obtain:

$$\frac{d\mathbf{g}}{dt} = \mathbf{J} \odot \mathbf{g} \quad (38)$$

where

$$\mathbf{J} = \frac{\partial \mathbf{g}}{\partial \mathbf{y}} = N \times N \text{ Jacobian matrix of } \mathbf{g} \text{ with respect to } \mathbf{y}. \quad (39)$$

Since the solution  $\mathbf{y}(t)$  and therefore  $\mathbf{J}(t)$  are both known functions of time, (38) can be considered a *linear* ODE (with known time-dependent coefficients) for  $\mathbf{g}$ . Taking the inner product of  $\mathbf{b}^i$  with (38) and using (21), we obtain:

$$\frac{df^i}{dt} = \sum_{j=1}^N \Lambda_j^i f^j, \quad i = 1, 2, \dots, N, \quad (40)$$

where

$$\Lambda_j^i \equiv \left[ \frac{d\mathbf{b}^i}{dt} + \mathbf{b}^i \odot \mathbf{J} \right] \odot \mathbf{a}_j, \quad i, j = 1, 2, \dots, N. \quad (41)$$

A set of basis vectors  $\mathbf{a}_i(t)$  is said to be *ideal* if (i) the inverse row vectors  $\mathbf{b}^i(t)$  can be accurately computed from (24) for all time interval of interest, (ii)  $\Lambda_j^i(t)$  is diagonal, and (iii) the diagonal elements of  $\Lambda_j^i(t)$  are ordered in descending magnitudes. For linear problems where  $\mathbf{J}$  is a constant matrix, the ideal basis vectors would be the (constant) ordered eigen-vectors of  $\mathbf{J}$ . For non-linear problems, the eigen-vectors of  $\mathbf{J}$  are time-dependent, and they do not diagonalize  $\Lambda_j^i$ .

## 5 The CSP Refinement of Basis Vectors

The method of CSP does not attempt to find the ideal set of basis vectors—even when  $\mathbf{g}$  is linear. Instead, it assumes that, at any moment in time, a

*trial* set of ordered basis vectors is somehow available, that the first  $M$  fastest modes are exhausted as measured by some criterion (to be specified later), and generates from this trial set a new *refined* set of basis vectors,  $\mathbf{a}_i^o$  and  $\mathbf{b}_i^o$ ,  $i = 1, 2, \dots, N$  using a two-step *refinement* procedure (Lam and Goussis, 1991a). When recursively applied, the refinement procedure successively weakens the coupling between the fast modes and the slow modes.

The step #1 refinement is:

$$\mathbf{b}_o^m(M) \equiv \mathbf{b}^m + \sum_{J=M+1}^N p_J^m(M) \mathbf{b}^J, \quad m = 1, 2, \dots, M, \quad (42a)$$

$$\mathbf{a}_J^o(M) \equiv \mathbf{a}_J - \sum_{n=1}^M \mathbf{a}_n p_J^n(M), \quad J = M+1, \dots, N. \quad (42b)$$

The step #2 refinement is:

$$\mathbf{b}_o^I(M) \equiv \mathbf{b}^I - \sum_{n=1}^M q_n^I(M) \mathbf{b}_o^n(M), \quad I = M+1, \dots, N, \quad (43a)$$

$$\mathbf{a}_m^o(M) \equiv \mathbf{a}_m + \sum_{J=M+1}^N \mathbf{a}_J^o(M) q_m^J(M), \quad m = 1, 2, \dots, M. \quad (43b)$$

The matrices  $p_J^m(M)$  and  $q_m^J(M)$  above are defined by:

$$p_J^m(M) \equiv \sum_{n=1}^M \tau_n^m(M) \Lambda_J^n, \quad m = 1, 2, \dots, M, \quad J = M+1, \dots, N, \quad (44a)$$

$$q_m^J(M) \equiv \sum_{n=1}^M \Lambda_n^J \tau_m^n(M), \quad m = 1, 2, \dots, M, \quad J = M+1, \dots, N, \quad (44b)$$

and  $\tau_m^n(M)$  is the inverse of  $\Lambda_m^n(M)$ :

$$\sum_{k=1}^M \tau_k^n(M) \Lambda_m^k(M) = \sum_{k=1}^M \Lambda_k^n(M) \tau_m^k(M) = \delta_m^n, \quad n, m = 1, 2, \dots, M. \quad (45)$$

The refinement procedure is readily programmable, and the refined basis vectors after each step satisfy the orthonormal relations, (24). It is essentially a generalization of the so-called “power method” for computing eigen-vectors, and produces a block diagonal  $\Lambda_i^i$  when converged.

The amplitude of the  $m$ -th fast mode satisfies the following differential equation (Lam and Goussis, 1991a):

$$\frac{df^m}{dt} = \sum_{n=1}^M \Lambda_n^m (f^m - f_\infty^m), \quad m = 1, 2, \dots, M, \quad (46a)$$

where

$$f_\infty^m \equiv - \sum_{J=M+1}^N p_J^n f^J, \quad m = 1, 2, \dots, M. \quad (46b)$$

$$f_o^m \equiv \mathbf{b}_o^m \odot \mathbf{g} = f^m - f_\infty^m, \quad m = 1, 2, \dots, M. \quad (46c)$$

Note that  $f_\infty^m$  is some linear combination of the trial slow mode amplitudes. Solving for  $f_\infty^m$  from (46c), we obtain:

$$f_\infty^m = f^m - f_o^m = (\mathbf{b}^m - \mathbf{b}_o^m) \odot \mathbf{g}, \quad m = 1, 2, \dots, M,$$

which shows clearly that  $f_\infty^m$  is proportional to the change of  $\mathbf{b}^m$  to  $\mathbf{b}_o^m$  as a consequence of the step #1 refinement procedure. In general,  $f_\infty^m$ , which is computed using the trial set of basis vectors, can not be considered “small.”

Let  $\tau(M)$  denote the magnitude of the time scale of the slowest of the fast modes. Let  $\tau(M+1)$  denote the magnitude of the currently active time scale. Theoretically, they can be estimated by the  $M$ -th and  $(M+1)$ -th eigen-values of  $\mathbf{J}$ . In the limit of small  $\tau(M)/\tau(M+1)$ —large time scale separation—the formal asymptotic solution of (46a) is:

$$f^m = f_\infty^m + f_{o,\infty}^m + \dots, \quad m = 1, 2, \dots, M, \quad (47a)$$

$$f_{o,\infty}^m \equiv \sum_{n=1}^M \tau_n^m(M) \frac{df_\infty^n}{dt}, \quad m = 1, 2, \dots, M. \quad (47b)$$

The order of magnitude of  $f_{o,\infty}^m$  can be estimated by:

$$f_{o,\infty}^m \approx O(f_\infty^m \tau(M)/\tau(M+1)), \quad m = 1, 2, \dots, M. \quad (48)$$

Assuming that  $\tau(M+1) \gg \tau(M)$ , the order of magnitude of  $f_{o,\infty}^m$  is now small in comparison to  $f_\infty^m$ —i. e. it is a “higher order” term. We have adopted the notation that superscript or subscript o indicates a variable evaluated with refined basis vectors. The above derivation can be found in Lam and Goussis (1991a).

Maas and Pope (1992) recognizes the importance of the eigen-vectors of  $\mathbf{J}$ , but recommends the use of its Schur vectors (Noble, 1988)—which transform  $\mathbf{J}$  into a lower-triangular form—as basis vectors. The advantage of Schur vectors for dealing with *dimensional* vectors is not clear.

## 5.1 The Trial Set of Basis Vectors

To get started, CSP needs to have a trial set of basis vectors. A number of options are available.

For sufficiently simple problems, one may wish to proceed analytically.  $N$  linearly independent stoichiometric vectors chosen from the reactions actually included in the full model (with supplementary basis vectors added as required) may be used as the default trial basis vectors. Educated guesses are then needed to establish the speed ranking of the modes.

A fool-proof procedure is to compute for the eigen-vectors of  $\mathbf{J}$  at  $t = 0$  and use them as time-independent trial basis vectors for  $t \geq 0$ . The reciprocal of the eigen-values, denoted by  $\tau(i)$ , is an approximate measure of the characteristic time scales of the modes. We shall assume that the  $\tau(i)$ 's are essentially real and are ordered in ascending magnitudes.

When the refinement process is performed numerically on a computer, the refined basis vectors used in the previous time-step can be used as the trial basis vectors for the new time-step. Under this strategy, the initial choice of trial basis vectors at  $t = 0$  is not critical.

## 5.2 The Number of Exhausted Modes

The refinement procedure requires the knowledge of  $M$ , the number of exhausted modes. In general, none of the fast modes are negligible at  $t = 0$  (*i.e.*  $M = 0$ ). As time progresses, the faster modes will eventually decay and become exhausted (*i.e.*  $f_o^m \rightarrow f_{o,\infty}^m$ ). The number of exhausted fast modes,  $M(t)$ , is determined by requiring that their contributions to  $\mathbf{g}$  (see (54) and (55a) later) over the next time interval of  $O(\tau(M+1))$  are negligible:

$$|\mathbf{a}_m^o f_o^m \tau(M)| < \mathbf{y}_{\text{error}}, \quad m = 1, 2, \dots, M, \quad (49a)$$

$$|\mathbf{a}_m^o f_{o,\infty}^m \tau(M+1)| < \mathbf{y}_{\text{error}}, \quad m = 1, 2, \dots, M, \quad (49b)$$

where  $\mathbf{y}_{\text{error}}$  is a dimensional column vector representing a user-specified threshold of absolute error allowed, and the vector inequality is individually enforced for *every* components of the vector. If one relaxes the requirement that the accuracy threshold for each component of  $\mathbf{y}$  be individually enforced, then the following are acceptable alternatives to (49a) and (49b):

$$|f_o^m| < O\left(\left|\frac{\mathbf{b}_o^m \odot \mathbf{y}_{\text{error}}}{\tau(M)}\right|\right), \quad m = 1, 2, \dots, M. \quad (49c)$$

$$|f_{o,\infty}^m| < O\left(\left|\frac{\mathbf{b}_o^m \odot \mathbf{y}_{error}}{\tau(M+1)}\right|\right), \quad m = 1, 2, \dots, M. \quad (49d)$$

Either of the above *exhaustion criterion* can readily be implemented computationally. The value of  $\tau(M+1)$  can be estimated by the current integration step-size selected by any automatic (explicit) ODE integration package. Note that the value of  $M$  need not be a monotonic function of time.

Actually, the exhaustion criterion for the so-called CSP radicals defined in §6.4 can be made more lenient when the so-called radical correction (to be discussed in §6.5 later) is applied. A full discussion of this subtle point, however, is beyond the scope of this paper.

For most problems, the desired time resolution  $\Delta t$  is usually known. If

$$\Delta t > \tau(M), \quad (50)$$

then the  $M$  fastest modes must be nearly exhausted in the  $\Delta t$  time scale of interest. If we are not interested in the details of what happens in the next  $\tau(M)$  seconds, we may use the simplified model with a non-zero value for  $M$  starting at  $t \approx 0$ , provided that we also adjust the initial conditions appropriately as demonstrated in (14) and (18). See §6.5 later.

### 5.3 The Refinement Process

The CSP refinement procedure consists of the following two steps.

1. Refinement of the fast row vectors using (42a) and the slow column vectors using (42b). This step depresses the magnitude of the upper-right block of  $\Lambda_K^m$ , ( $m = 1, \dots, M$ ,  $K = M + 1, \dots, N$ ), by the factor  $\tau(M)/\tau(M+1)$ , and thus weakens the coupling of the fast mode amplitudes from the slow.
2. Refinement of the slow row vectors using (43a) and the fast column vectors using (43b). This step depresses the magnitude of the lower-left block of  $\Lambda_m^K$ , ( $K = M + 1, \dots, N$ ,  $m = 1, \dots, M$ ), by the factor  $\tau(M)/\tau(M+1)$ , and thus weakens the coupling of the slow mode amplitudes from the fast.

The full cycle of the two-step refinement process renders the new  $\Lambda_j^i$  matrix calculated from the refined basis vectors more nearly block diagonal

than before. Step #1 improves the accuracy of the simplified model, while step #2 ensures that the simplified model is not stiff. The speed ranking of the modes can be estimated by the diagonal elements of the  $\Lambda_j^i$  matrix.

In our example in §3.3, the set of alternative basis vectors (28a), (28b) and (28c) used was obtained by adopting (25a), (25b) and (25c) as the ordered trial set, and then refining them analytically through step #1 using  $M = 1$ . We obtain:

$$\mathbf{b}_o^1 = \frac{1}{K_1 + 4A} [-2A, \quad K_1, \quad 0]^T, \quad (51a)$$

$$\mathbf{a}_2^o = \frac{1}{K_1 + 4A} [K_1, \quad 2A, \quad (K_1 + 4A)\Delta H_2 - (K_1 + 2A)\Delta H_1]^T, \quad (51b)$$

$$\mathbf{a}_3^o = [0, \quad 0, \quad 1]^T. \quad (51c)$$

These refined vectors are significantly modified from their trial counterparts. Performing step #2, we obtain:

$$\mathbf{b}_o^2 = [1 + \frac{2A\epsilon}{K_1 + 4A}, \quad 2 - \frac{K_1\epsilon}{K_1 + 4A}, \quad 0], \quad (52a)$$

$$\mathbf{b}_o^3 = [\Delta H_1 - \Delta H_2, \quad \Delta H_1 - 2\Delta H_2, \quad 1], \quad (52b)$$

$$\begin{aligned} \mathbf{a}_o^1 = [-2 + \frac{K_1\epsilon}{K_1 + 4A}, \quad 1 + \frac{2A\epsilon}{K_1 + 4A}, \\ \Delta H_1 - (\frac{K_1 + 2A}{K_1 + 4A}\Delta H_1 - \Delta H_2)\epsilon], \end{aligned} \quad (52c)$$

where  $\epsilon$  is a dimensionless parameter defined by

$$\epsilon \equiv \frac{k_2(K_2 + 2)}{k_1(K_1 + 4A)}. \quad (53)$$

These refined vectors are only slightly modified from their trial counterparts for  $\epsilon \ll 1$ . Generally speaking, whenever the set of trial  $\mathbf{a}_i$  basis vectors are intelligently chosen, step #2 will provide only small corrections. If the trial set was randomly chosen, more than one full cycle of the two-step refinement process may be necessary to generate the correct leading order result in the limit of  $\epsilon \rightarrow 0$ .

The trial set is usually chosen initially to be time-independent for the sake of convenience. For non-linear problems, the refined set will in general



be time-dependent, and the associated time derivatives in  $\Lambda_j^i$  must be properly evaluated. Analytically, this is a straightforward step which could be quite tedious algebraically. From the programming point of view, however, good approximation to  $db^i/dt$  can be obtained in a number of ways, such as utilizing the availability of stored values in the previous time steps and/or the predicted values in the next time step used in most integration routines.

## 6 Using the Refined Basis Vectors

Using the refined basis vectors, the governing system of ODE's become:

$$\frac{dy}{dt} = \mathbf{g}_o^{o,fast} + \mathbf{g}_o^{o,slow} \quad (54)$$

where

$$\mathbf{g}_o^{o,fast} \equiv \sum_{m=1}^M \mathbf{a}_m^o f_o^m = \left( \sum_{m=1}^M \mathbf{a}_m^o \mathbf{b}_o^m \right) \odot \mathbf{g}, \quad (55a)$$

$$f_o^m = \mathbf{b}_o^m \odot \mathbf{g}, \quad m = 1, 2, \dots, M, \quad (55b)$$

$$\mathbf{g}_o^{o,slow} = \mathbf{g} - \mathbf{g}_o^{o,fast} = \sum_{r=1}^R \mathbf{s}_{o,r}^{o,slow} F^r, \quad (55c)$$

$$\mathbf{s}_{o,r}^{o,slow} \equiv \left( \mathbf{I} - \sum_{m=1}^M \mathbf{a}_m^o \mathbf{b}_o^m \right) \odot \mathbf{s}_r, \quad r = 1, 2, \dots, R. \quad (55d)$$

The column vector  $\mathbf{s}_{o,r}^{o,slow}$  is mathematically the projection of  $\mathbf{s}_r$  in the so-called *slow subspace* or *manifold*, and can be interpreted physically as the *effective stoichiometric vector* of the  $r$ -th elementary reaction. Unlike the original chemical  $\mathbf{s}_r$ , the components of  $\mathbf{s}_{o,r}^{o,slow}$  are not necessarily integers or rational numbers, and may involve species which do not appear in  $F^r(\mathbf{y})$ .

When the  $M$  fast modes satisfy the exhaustion criterion described in the next section, the simplified model is simply:

$$\frac{dy}{dt} \approx \mathbf{g}_o^{o,slow} \quad (56a)$$

$$= \sum_{K=M+1}^N \mathbf{a}_K^o f_o^K. \quad (56b)$$

## 6.1 Classification of Modes

In general, there are three kinds of modes: exhausted modes, currently active modes, and dormant modes. Let  $\tau(i)$  represent the characteristic time scale of the  $i$ -th mode. It is assumed that:

$$\tau(m) \ll \tau(K), \quad m = 1, 2, \dots, M, \quad K = M + 1, \dots, N. \quad (57)$$

The ordering among  $\tau(m)$  and  $\tau(K)$  is not important.

**Exhausted Modes:** By applying the exhaustion criterion (49b), the number  $M$  of exhausted fast modes is determined, yielding a set of  $M$  approximate equations of state:

$$f_o^m = \mathbf{b}_o^m \odot \mathbf{g} = \sum_{r=1}^R B_{o,r}^m F^r \approx 0, \quad m = 1, 2, \dots, M, \quad (58)$$

where

$$B_{o,r}^i \equiv \mathbf{b}_o^i \odot \mathbf{s}_r, \quad i = 1, 2, \dots, N, \quad r = 1, 2, \dots, R. \quad (59)$$

**Currently Active Modes:** The remaining  $N - M$  modes are kept in (56b). Using (55c), we rewrite the simplified model as follows:

$$\frac{d\mathbf{y}}{dt} \approx \sum_{r=1}^R \mathbf{s}_{o,r}^{o,slow} F^r \quad (60)$$

Equation (60) can be numerically integrated without the need of a stiff solver. The integration time-step used should be a fraction of  $\tau(M + 1)$ , the characteristic time scale of the  $(M + 1)$ th mode. The initial condition of (60) must satisfy (58) in the sense of (49c). If the initial trial fast column basis vectors were randomly chosen, the accuracy of (60) is  $O((\tau(M)/\tau(M + 1))^c)$  where  $c$  is the number of full two-step refinement cycles. If they were initially “intelligently” chosen, then  $c$  is the number of step #1 refinements.

**Dormant Modes:** The amplitude of some of the slow modes kept in (56b) may be extremely small or even identically zero. When a slow mode is deemed negligible—when the its contribution to  $\mathbf{g}_o^{o,slow}$  in the current

time period is estimated to be less than  $\mathbf{y}_{error}$  component by component, it is said to be a *dormant mode*. In the example, mode #3 is a permanent dormant mode. If mode #N is a dormant mode, then:

$$f_o^N = \mathbf{b}_o^N \odot \mathbf{g} \approx 0, \quad (61)$$

or,

$$f_o^N = \sum_{r=1}^R B_{o,r}^N F^r \approx 0. \quad (62)$$

However, unlike (58), (62) is *not* a useful equation—it *can not be used as an approximate equation of state*. Instead, (61) is the more useful equation, indicating that the vector  $\mathbf{g}$  has negligible projection in a specific “direction.” If  $\mathbf{b}_o^N$  can be shown to be the gradient of a scalar—a condition known as *holonomic constraint* in classical mechanics—then that scalar is a conserved “integral of motion.” Conservation laws of atomic species manifests themselves as permanent dormant modes with *constant* row vectors (which are always holonomic). Equation (33c) is a conservation law since  $\mathbf{b}^3$  is holonomic and  $f^3$  is identically zero.

The solution of (60) automatically satisfy (58), (61) and (62). The distinction between (58) and (61) will be further discussed later.

## 6.2 Equation of State and Participation Index

The left-hand side of (58) usually consists of large positive and negative terms which nearly cancel each other. Which elementary reactions participate most strongly in this balancing act? The *participation index*, denoted by  $P_{r,o}^i$ , is designed to provide this information and is defined as follows:

$$P_{r,o}^i \equiv \frac{B_{o,r}^i F^r}{\sum_{r=1}^R |B_{o,r}^i F^r| + \left| \frac{\mathbf{b}_o^i \odot \mathbf{y}_{error}}{\tau(M+1)} \right|}, \quad i = 1, 2, \dots, N, \quad r = 1, 2, \dots, R. \quad (63)$$

where it is assumed that forward and reverse reactions are counted as distinct so that no cancellation occurs within any  $F^r$ .  $P_{r,o}^i$  is a measure of the participation of the r-th elementary reaction to the balancing act of the i-th

mode. To get an idea of which elementary reactions are the major participants of each fast mode, we just need to sort the elementary reactions by their participation indices. A exhausted fast mode usually has several significant participation indices, a slow dormant mode may not have any, while a permanently dormant mode representing a conservation law has none. In our example worked out in §3.3, the participation index data for mode #1 will show that reaction #1 is the main participant of  $f^1$  as defined by (30a), reaction #2 is the main participant of  $f^2$  as defined by (30b), while  $f^3 = 0$  has no participant at all and can be interpreted as a conservation law.

### 6.3 Simplified Model and Importance Index

The right-hand side of (60) consists of terms which control the reaction rate of the system. For each component of the state vector  $\mathbf{y}$ , we can order the terms on the right-hand side in descending magnitudes. Which elementary reactions are most important in controlling the reaction rate of a particular species of interest? The *importance index*, denoted by  $I_r^{i,o}$  and designed to provide this information, is defined as follows:

$$I_{o,r}^{i,o} \equiv \frac{s_{o,r}^{i,o,slow} F^r}{\sum_{r=1}^R |s_{o,r}^{i,o,slow} F^r| + \left| \frac{y_{error}^i}{\tau(M+1)} \right|}, \quad i = 1, 2, \dots, N, \quad r = 1, 2, \dots, R. \quad (64)$$

$I_{o,r}^{i,o}$  is a measure of the relative importance of the contribution of the  $r$ -th elementary reaction to the current reaction rate of the  $i$ -th species. Note that if  $I_r^{i,o}$ 's were computed using the default  $s_r$ 's, we would obtain the misleading information that the fast reactions are rate-controlling even after they are exhausted. In general, the values of the importance indices change discontinuously at the moment when a new fast mode is declared exhausted—the  $I_{o,r}^{i,o}$ 's of the major participants in the new exhausted mode will drop, while those in the emerging rate-controlling modes will rise. In the example worked out in §3.3, the importance index data on (36) computed using  $s_{o,r}^{o,slow}$  (see §7.5) will show that reactions #1 and #2 are important in controlling the overall reaction rate but each in their own time period only.

## 6.4 The Radical Pointer

When  $M$  modes are exhausted,  $M$  algebraic equations are obtained from (58) which can be used to replace  $M$  of the ODE's in the subsequent epochs. The question is: *which* ODE's can be replaced? In other words, which species are the radicals?

CSP associates with each exhausted mode one or more species by the *radical pointer*. The radical pointer of the  $m$ -th mode,  $Q_m(i)$ , is defined by the  $N$  diagonal elements of the  $N \times N$  matrix  $\mathbf{a}_m \mathbf{b}^m$ , refined basis vectors preferred. Geometrically, the magnitude of  $Q_m(i)$ , which is dimensionless and its sum over  $i$  is unity, is a measure of how “perpendicular” the  $i$ -th species axis is to the surface defined by the  $m$ -th equation of state in  $y$  space. A species  $k$  is identified as a *CSP radical* associated the  $m$ -th exhausted mode whenever  $Q_m(k)$  is not a small number.

For the example treated in §3.3, we have for mode #1:

$$\mathbf{a}_1 \mathbf{b}^1 = \frac{1}{K_1 + 4A} \begin{pmatrix} 4A & -2K_1 & 0 \\ -2A & K_1 & 0 \\ -2A\Delta H_1 & K_1\Delta H_1 & 0 \end{pmatrix}. \quad (65)$$

The set of its diagonal elements is the radical pointer:

$$Q_1(i) = \frac{1}{K_1 + 4A} [4A, \quad K_1, \quad 0]. \quad (66)$$

This radical pointer informs us that either A or B, but definitely not C, may be used as a radical. In other words, only the ODE of either A or B can be replaced by (35b).

Maas and Pope (1992) did not realize that the choice of what species to solve for from the equations of state is restricted, and suggested that they “...can be chosen quite arbitrarily” with special caution on uniqueness of solutions. This is not our experience (Lam and Goussis, 1991b), and (66) is developed to provide a quantitative criterion for radicals. We have tested our radical pointer criterion by purposely solving for the “wrong” species—according to our radical pointer—from (58) in a number of test problems, and obtained wrong answers as expected.

## 6.5 The Radical Correction

What if the values of  $f_o^m$  in (58) are small but not as small as we would like at some moment in time? Theoretically, all  $M$  modes should rapidly decay to some much smaller values in the next several  $\tau(M)$  seconds, while the main reaction activity proceeds with the current characteristic time scale of  $\tau(M+1)$  seconds. If we are not interested in the details of the decay process but are only interested in finding an approximate “initial” condition for the next time period, we can use Newton’s method to find the change to the value of  $\mathbf{y}$ ,  $\Delta\mathbf{y}_{rc}$ , which would zero out the values of  $f_o^m$ ,  $m = 1, 2, \dots, M$ :

$$\Delta\mathbf{y}_{rc} \approx - \sum_{m,n=1}^M \mathbf{a}_m^o \tau_n^m f_o^n. \quad (67)$$

In other words,  $\mathbf{y} \rightarrow \mathbf{y} + \Delta\mathbf{y}_{rc}$  as the amplitudes of the fast modes decay toward zero in the next several  $\tau(M)$  seconds. We shall call  $\Delta\mathbf{y}_{rc}$  the *radical correction*. In Lam and Goussis (1991a), the radical correction was referred to as “inclusion of the homogeneous solution” in evaluating the change of  $\mathbf{y}$ , but no details were given there.

When a simplified model is used to compute for an approximation solution by neglecting the  $M$  exhausted modes, the values of  $f_o^m$ ’s are small at the beginning of the time period and are theoretically expected to remain small in the slow evolutionary period. The radical correction can be used to ensure that the numerical solutions adequately satisfy the approximate equations of state as required.

Suppose the initial values in the example worked out in §3.3 does not satisfy the partial-equilibrium of mode #1:

$$f_o^1(0) = F^1(0) + \frac{K_1 + 2A(0)}{K_1 + 4A(0)} F^2(0) \neq 0, \quad (68)$$

and the solution in the rapid transient period is of no interest to the investigator. The radical correction can be used to obtain the effective initial values, the counter part of (14), for the next time period. With  $M = 1$ ,  $\tau_1^1 = -(k_1(K_1 + 4A(0)))^{-1}$ , (67) gives:

$$A(0+) \approx A(0) - \frac{2f_o^1(0)}{k_1(K_1 + 4A(0))}, \quad (69a)$$

$$B(0+) \approx B(0) + \frac{f_o^1(0)}{k_1(K_1 + 4A(0))}, \quad (69b)$$

$$C(0+) \approx C(0) + \frac{\Delta H_1 f_o^1(0)}{k_1(K_1 + 4A(0))}. \quad (69c)$$

It can easily be verified that (10) is satisfied and  $A + 2B$  is unchanged by this radical correction, while the new value of  $f_o^1(0+)$  becomes much smaller than before. By recursive applications  $A(0+)$  will converge to (14), and  $f_o^1(0+)$  will converge to the nearest stable zero. The computation for the slow evolutionary time period can now commence with (36) with the new initial values.

## 6.6 Explosive Modes

For chemical kinetics, the eigen-values of  $\mathbf{J}$  are usually real, and mostly negative, signifying decaying modes. Occasionally, some modes may have positive eigen-values, signifying "*explosive modes*" which are often of interest in the study of "ignition" mechanisms (Trevino and Solorio, 1991; Trevino, 1991). In our example, whenever  $A < K_1/(2K_2)$  an explosive mode exists which is clearly the manifestation of the *chain branching* of the  $B$  radical in the reaction system.

Because the matrix  $\Lambda_j^i$  is not exactly block diagonal, the non-zero coupling between the fast exhausted modes and the slow explosive modes can cause some exhausted modes to come alive again. From the point of view of computation and programming, this complication is easily handled.

## 6.7 The Minimum System

Using the participation and importance indices, it is a simple matter to identify the minimum set of species and unknowns (ignore the unimportant reactants but includes any species of special interest to the investigator) and the minimum set of elementary reactions (ignore the unimportant reactions) to form a minimum reduced reaction system which can represent  $\mathbf{g}$  to any reasonable desired user-specified threshold of accuracy for any time period(s) of interest.

## 7 Comments on CSP

In terms of elegance, there is no substitute for a conventional asymptotic analysis of an appropriately non-dimensionalized problem with a well defined small parameter  $\epsilon$ , with analytical results expressed in terms of simple functions.

In dealing with practical problems, there exists few guidelines for order of magnitude estimates and the intelligent non-dimensionalization of the variables. The identification of the small parameter  $\epsilon$  is also not straightforward; for a real problem it may be insufficiently small even when successfully identified. For moderately complex reaction systems, the formalism of asymptotics must be replaced by *ad hoc* quasi-steady and/or partial-equilibrium hypothesis, and the role of experience and intuition then becomes central. With sufficient algebraic skill, such methodology is indeed capable of generating analytical results. However, for massively complex reaction systems, this option is simply not viable.

The theory of CSP provides a new formalism to do asymptotics. Most importantly, it does not require non-dimensionalization of the variables and the identification of a small parameter. The time-dependent value of  $\tau(M)/\tau(M+1)$  is the small parameter. The CSP algorithm can be performed analytically for sufficiently simple problems, as was demonstrated in §3.3, and it can be programmed to handle massively complex problems—provided the fast modes are of the boundary layer type and decay with time eventually.

CSP can be used to test an intuitive guess, provides a fool-proof way to obtain the correct leading approximation in the absence of good ideas, and allows the theoretician to concentrate on the task of extracting physical insights—because all the massively complicated algebra are left to be performed numerically on the computer.

In most cases, it is relatively easy to interpret a CSP-generated equation of state as either a partial-equilibrium or a quasi-steady approximation. However, there are also situations when such interpretation is not immediately obvious, and the CSP data becomes physically sensible only after further reflections.

From the point of view of asymptotics, CSP is distinctly different from the conventional analytical method of “matched asymptotic expansions,” for no asymptotic matching is required. A detailed discussion of the differences, however, is beyond the scope of this paper.



### 7.1 Local-Eigen Vectors vs. Refined Basis vectors

As mentioned previously, the set of local eigen-vectors of  $\mathbf{J}$  is a fool-proof choice for use as trial basis vectors. In fact, the special set of basis vectors ((28a), (28b) and (28c)) used in §3.3 is the leading order approximation of the right eigen-vectors of  $\mathbf{J}$ , with  $k_2K_2/k_1K_1$  playing the role of a small parameter. If only so-called leading order approximation (for sufficiently small  $k_2K_2/k_1K_1$ ) is desired, this set is totally adequate. But what if the value of  $k_2K_2/k_1K_1$  of practical interest is only 0.15, and it is desired to develop a simplified model with accuracy around 3%? The CSP refinement procedure can be recursively applied to improve the accuracy.

The CSP theory formally guarantees that each full cycle of refinement increases the accuracy of the simplified model by the factor  $\tau(M)/\tau(M+1)$ . In the first full cycle, we can generate the leading approximation by using constant trial vectors so that no time derivatives are included. In most cases, the leading approximation to a complex problem is adequate to provide most physical insights. The second full cycle needs the evaluation of first time derivatives, and the third full cycle needs the evaluation of second time derivatives, *etc.* Mathematically, these time derivatives are all available. Hence CSP is capable of significantly higher accuracy than using just the local eigen-vectors. It is, of course, not at all necessary to use the local eigen-vectors as trial basis vectors; any informed, intelligent guess can be used. In a computer code, it is possible to implement two full refinement cycles using relatively little computational resource.

To continue beyond §3.3, we may choose (28a), (28b) and (28c) as our time-dependent trial set, respecting the presence of  $A(t)$  in  $\mathbf{a}_2$  and  $\mathbf{b}^1$ . This (second) refinement proceeds routinely except that the time derivative term in (41) must be included in evaluating  $\Lambda_j^i$ . The new CSP-derived simplified models so generated will be accurate to  $O(k_2K_2/k_1K_1)^2$ , compared to  $O(k_2K_2/k_1K_1)$  for the results obtained earlier. One more cycle of refinement will generate models of accuracy  $O(k_2K_2/k_1K_1)^3$ , *etc.*

### 7.2 Equation of State and Conservation Law

In the combustion literature, the concept of conserved scalars is linked with the assumption of equal mass diffusivity coefficients and unity Lewis numbers. Since no diffusion effects are considered here, these requirements become

irrelevant. In this section, we shall show how (approximate) conserved scalars for such systems can be found as a by-product of CSP.

Taking the dot product of  $\mathbf{b}_o^i$  with (54), we have:

$$\mathbf{b}_o^i \odot \frac{d\mathbf{y}}{dt} = f_o^i, \quad i = 1, 2, \dots, N. \quad (70)$$

If a row vector  $\mathbf{b}_o^n$  can be expressed as the gradient (with respect to  $\mathbf{y}$ ) of a scalar function  $\Theta_{n,o}(\mathbf{y})$  times a scalar function  $\theta_{n,o}(\mathbf{y})$ , then the mode shall be called an *holonomic* mode—a concept well known in classical mechanics. The corresponding equation is (70) is called an *holonomic constraint*, and can be rewritten as:

$$\theta_{n,o} \frac{d\Theta_{n,o}}{dt} = f_o^n, \quad \text{selected } n\text{'s}. \quad (71)$$

We shall call  $\Theta_{n,o}$ , when it exists, an *eligible conserved scalar*.

When the  $m$ -th fast mode becomes exhausted, an equation of state is obtained by setting  $f_o^m \approx 0$ . If this mode is also holonomic, the associated eligible conserved scalar  $\Theta_{m,o}$  then becomes a *exhausted conserved scalar*—its value remains constant from the moment of exhaustion. It is likely that all exhausted refined fast modes are holonomic, and that  $\Theta_{m,o}$  and  $f_o^m$  are linearly dependent—thus no new information is provided by the exhausted conserved scalars.

When the amplitude of the  $K$ -th slow mode is found “negligible,” setting this dormant mode  $f_o^K \approx 0$  yields no information at all. We can only conclude from (70) that the component of the vector  $d\mathbf{y}/dt$  “in the the direction of  $\mathbf{a}_K^o$ ” is negligible. However, if this dormant mode is holonomic (*e. g.*  $\mathbf{b}_o^K$  are constants, yielding  $\theta_{K,o} = 1$ ,  $\Theta_{K,o} = \mathbf{b}_o^K \odot \mathbf{y}$ ), then the associated  $\Theta_{K,o}$  is a *dormant conserved scalar*—its value is approximately conserved whenever the  $K$ -th mode is dormant. Conserved scalars in the combustion literature are dormant ones, and they almost always have simple physical meanings, such as conservation of atomic species or total energy. While  $\Theta_{K,o} \approx \text{constant}$  is also an algebraic relation between the species, we do *not* call it an equation of state because the *constant* is not universal.

In our example, the basis vectors used in §3.3 are the leading order results obtained by refining the trial basis vectors given in §3.2. Equations (33a), (33b) and (33c) correspond to (70) and they are all holonomic. The eligible

conserved scalars are ( $M = 1$ ):

$$\Theta_{1,o} = -A^2 + K_1 B, \quad (72a)$$

$$\Theta_{2,o} = A + 2B, \quad (72b)$$

$$\Theta_{3,o} = (\Delta H_1 - \Delta H_2)A + (\Delta H_1 - 2\Delta H_2)B + C, \quad (72c)$$

with

$$\theta_{1,o} = \frac{1}{K_1 + 4A}, \quad \theta_{2,o} = 1, \quad \theta_{3,o} = 1. \quad (73)$$

All three refined modes in this example are exactly holonomic. In general, there is no guarantee that any CSP refined mode is holonomic<sup>4</sup>—it is not possible to determine from numerical CSP data whether a mode is holonomic or to deduce the form of the possible eligible conserved scalar except for the obvious case of time-independent  $\mathbf{b}_o^n$ .

### 7.3 The User-Specified $\mathbf{y}_{error}$

The role of a theory is to construct a model which should be as simple as possible and yet can generate valid predictions in some domain of the parameter space of interest. A good model need not predict *all* things correctly. For example, a certain simplified model may be very good indeed for the heat release and temperature history, but very bad for the predictions of certain pollutant concentrations. For the same reaction system, different simplified models may be appropriate depending on the desired scope and accuracy of the solutions.

The CSP theory addresses this issue by choosing not to directly define a vector norm for the  $N$ -dimensional state space of  $\mathbf{y}$ . Instead, it asks the investigator to supply the vector  $\mathbf{y}_{error}$ , which specifies the amount of absolute error considered tolerable for each component of  $\mathbf{y}$ . This step is intuitively sensible, and is conceptually equivalent to choosing a norm. The CSP theory relies on this  $\mathbf{y}_{error}$  to decide whether a decaying fast mode should be neglected. As a consequence, a CSP-derived simplified model which focuses

---

<sup>4</sup>A sufficient but *not* necessary condition for the  $n$ -th mode to be holonomic is that  $\mathbf{b}^n = \text{constant}$ . Hence constant trial row basis vectors always generate holonomic modes, but the resulting eligible conserved scalars may never become conserved scalars. For our example, if the default trial  $\mathbf{b}^1$  in §3.2 were used, we would obtain  $\Theta_1 = -A - B$  which, in contrast to  $\Theta_{1,o}$ , is not conserved after fast mode #1 is exhausted.

on temperature only may be quite different from one which claims additional predictive capability such as pollutant concentrations.

If too stringent a  $y_{\text{error}}$  is chosen, CSP would simply report  $M = 0$  and would fail to recommend any simplified model. As  $y_{\text{error}}$  becomes more forgiving, CSP would recommend simpler models consistent with the specified tolerance. This posture of producing simplified models on demand is refreshing—when compared to the posture of conventional asymptotics.

## 7.4 Insights from CSP Numbers

In a theoretical analysis, no specific numerical values of the parameters in the problem need be specified; only their order of magnitude is assumed. While the accuracy of the analysis may be limited—because the small parameter may not be that small in practice—the parametric dependence of the results are available for inspection and interpretation. An experienced theoretician can speak knowledgeably about the reaction system and interpret the analytical results in physically meaningful and intuitive terms such as chain branching, radical formation, ignition temperature, alternative reaction paths, *etc.*

When results are obtained computationally, each set of numerical data is valid only for one specific set of parameters. For massively complex problems, the computer printouts are overwhelming. The interpretation of these numbers is a much more difficult matter. The CSP data generated, which is all numerical, is designed to be easy to use to extract qualitative and physically meaningful insights.

For non-linear problems, the CSP data is itself massive. However, it need not be computed at every time step; it is needed only when the theoretician wants to know: what is going on here? While the time dependence of the reaction system may appear to be very complex, the CSP-derived refined basis vectors may depend only weakly on time, and the simplified model derived at selected points in time can provide insights about the “physical mechanism” of the system for a finite time interval. In fact, significant change of the behaviors of basis vectors is a signal that the physical mechanism has changed, and a new simplified model is needed. For linear problems, a single set of CSP data—the eigen structure of the constant matrix  $J$ —will explain everything for all time. For our simple example (which is non-linear), a single set of time-independent trial basis vector is adequate to generate the correct

refined set for all time.

From the CSP viewpoint, the problem of simplified kinetics modeling reduces to finding a set of basis vectors which make  $\Lambda_j^i$  block-diagonal. The conventional methods guess at them, while CSP provides a rational and programmable way of refining a trial set to make the resulting  $\Lambda_j^i$  more diagonal than before. For massively complex problems, the computer is assigned the task of computing an adequate set, and the investigator uses common sense to extract physically interesting information from the computer generated numerical basis vectors. The participation index and the importance index are provided to quantify the roles played by each elementary reaction included in the model. Together they provide answers to most of the interesting questions about a reaction system. Any simplified model derived based on intuition and experience can now be compared with the CSP-derived results to verify that the various judgments and guesses used are correct.

Depending on the user-specified accuracy threshold,  $y_{error}$ , certain chemical species and elementary reactions can be removed from the reaction system, producing the so-called reduced reaction system. The more lenient  $y_{error}$  is, the simpler the CSP-derived reduced system—while the essential character of the full system is retained. In Goussis and Lam (1992), the methanol oxidation problem was studied with 30 species plus temperature and 173 elementary reactions. The CSP data generated can be roughly divided into four epochs, each characterized by a distinctly different set of CSP-derived basis vectors, and together they indicated (through the CSP indices) that a reduced reaction system with 15 species (including methanol) would have adequate accuracy for all 15 unknowns. This CSP-derived insight was computationally confirmed. This reduced reaction system, of course, makes no predictions on the discarded species.

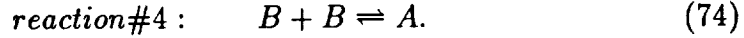
## 7.5 CSP vs. Sensitivity Analysis

The standard method of sensitivity analysis (Yetter, Dryer and Rabitz, 1991) is to linearize the problem and then to compute for the linearized response to various perturbations. For example, if one wishes to know what happens to  $y^{95}$  when  $k_{127}$  is changed by a small amount, one numerically computes  $d(\log y^{95})/d(\log k_{127})$ .

CSP provides an alternative to this brute-force method. First, we look at the participation indices  $P_{127,o}^m$ ,  $m = 1, 2, \dots, M$ . If these indices indicate

that reaction #127 is a significant participant of the  $m$ -th exhausted fast mode, then  $k_{127}$  will directly affect the values of the radicals pointed to by the radical pointer  $Q_m(i)$ . Otherwise  $k_{127}$  has no effect on the radicals. Next, we look at the importance index  $I_{o,127}^{95,o}$ ; its numerical value tells us how strongly  $k_{127}$  affects the reaction rate of  $y^{95}$ .

Frequently, it is desired to know what would happen if additional elementary reactions were added to a reaction system after a computation is already done. CSP can be used to provide useful answers. To illustrate, let reaction #4 be added to our example reaction system:



Its stoichiometric vector and reaction rate are:

$$\mathbf{s}_4 = [1, \quad -2, \quad \Delta H_4]^T, \quad F^4 = k_4(B^2 - K_4 A). \quad (75)$$

Since  $\mathbf{s}_4$  is not linearly independent, we have:

$$\mathbf{s}_4 = \mathbf{s}_1 - 3\mathbf{s}_2 - (\Delta H_1 - 3\Delta H_2 - \Delta H_4)\mathbf{s}_3. \quad (76)$$

Hence:

$$B_4^i = B_1^i - 3B_2^i - (\Delta H_1 - 3\Delta H_2 - \Delta H_4)B_3^i, \quad (77)$$

$$\mathbf{s}_{o,4}^{o,slow} = \mathbf{s}_{o,1}^{o,slow} - 3\mathbf{s}_{o,2}^{o,slow} - (\Delta H_1 - 3\Delta H_2 - \Delta H_4)\mathbf{s}_{o,3}^{o,slow}. \quad (78)$$

Using the basis vectors in §3.3, we can computed the following CSP data:

$$B_1^1 = 1, \quad B_2^1 = \frac{K_1 + 2A}{K_1 + 4A}, \quad B_3^1 = 0, \quad (79a)$$

$$B_1^2 = 0, \quad B_2^2 = 1, \quad B_3^2 = 0, \quad (79b)$$

$$B_1^3 = 0, \quad B_2^3 = 0, \quad B_3^3 = 1, \quad (79c)$$

and (for the time period when  $M = 1$  only),

$$\mathbf{s}_{o,1}^{o,slow} = [0, \quad 0, \quad 0]^T, \quad (80a)$$

$$\mathbf{s}_{o,2}^{o,slow} = \frac{1}{K_1 + 4A} [K_1, \quad 2A, \quad (K_1 + 4A)\Delta H_2 - (K_1 + 2A)\Delta H_1]^T, \quad (80b)$$

$$\mathbf{s}_{o,3}^{o,slow} = [0, \quad 0, \quad 1]^T. \quad (80c)$$

The effective stoichiometric vectors for the other two time periods are also available. It is now a simple matter to compute the participation and importance indices for reaction #4 from this CSP data and decide whether its previous omission can be justified in any time period of interest. If the indices  $P_{4,o}^i$  and  $I_{4,o}^i$  show that reaction #4 is a major player, then the old basis vectors should be refined to reflect the new character of the new reaction system.

## 7.6 Effects on Diffusion

If spatial diffusion is included, the governing equations will contain the Laplacian operator, and become a system of PDE's:

$$\frac{dy}{dt} = \mathbf{g} + \mathbf{D} \odot \nabla^2 \mathbf{y} \quad (81)$$

where  $\mathbf{D}$  is—in most cases—a  $N \times N$  diagonal matrix of diffusion coefficients which are considered constants here for the sake of simplicity.

Assuming that the spatial diffusion mechanism is not the fastest process, we can obtain the corresponding approximate equations of state, (58), when the fastest  $M$  modes are exhausted as before. In the slow evolutionary time period and spatial domain, the fast modes can be neglected from the right-hand side of (81) to obtain, instead of (60), the following simplified model:

$$\frac{dy}{dt} \approx \sum_{r=1}^R \mathbf{s}_{o,r}^{o,slow} F^r + \mathbf{D}_o^o \odot \nabla^2 \mathbf{y} \quad (82)$$

where  $\mathbf{D}_o^o$  is the *effective diffusion matrix*, the projection of  $\mathbf{D}$  in the slow subspace, given by:

$$\mathbf{D}_o^o \equiv (\mathbf{I} - \sum_{m=1}^M \mathbf{a}_m^o \mathbf{b}_o^m) \odot \mathbf{D}. \quad (83)$$

Let the diffusion matrix  $\mathbf{D}$  in our example be diagonal, with  $D_A$ ,  $D_B$ , and  $D_C$  as the diagonal elements:

$$\mathbf{D} = \begin{pmatrix} D_A & 0 & 0 \\ 0 & D_B & 0 \\ 0 & 0 & D_C \end{pmatrix}. \quad (84)$$

When  $M = 1$ , the effective diffusion matrix  $\mathbf{D}_o^\circ$  can be computed from (83) and (65):

$$\mathbf{D}_o^\circ = \frac{1}{K_1 + 4A} \begin{pmatrix} K_1 D_A & 2K_1 D_B & 0 \\ 2AD_A & 4AD_B & 0 \\ 2A\Delta H_1 D_A & -K_1\Delta H_1 D_B & (K_1 + 4A)D_C \end{pmatrix}. \quad (85)$$

This derivation of  $\mathbf{D}_o^\circ$  using CSP basis vectors is straightforward and programmable, and can be used to deal with massively complex PDE systems. Adjacent to solid boundaries, spatial boundary layers will exist, and *effective boundary values* for (82) are needed and must be carefully derived.

## 8 Discussion

Experience and intuition have always been central to the conventional derivation of simplified models. It was generally known that both the partial-equilibrium and the quasi-steady approximations were related to conventional analytical singular perturbation procedures—provided that the relevant small parameter(s) could be identified.

The goal of developing a general theory of singular perturbation which can handle any system of non-linear first order ODE's in a programmable manner without the identification of small parameter(s) seems very ambitious indeed. The CSP theory developed by Lam *et. al.* has achieved this goal, but only for *boundary-layer type* problems where all fast modes eventually decay exponentially. Fortunately, most problems in chemical kinetics are of this type.

The basic strategy of CSP is to uncouple the fast, exhausted modes from the slower, currently active modes through an intelligent choice of basis vectors. For a strictly linear problem, the ideal uncoupling basis vectors are the time-independent eigen-vectors of  $\mathbf{J}$ . For non-linear problems, the desired uncoupling basis vectors are time-dependent because  $\Lambda_j^i$  depends on  $\mathbf{y}(t)$ . The main concession made by CSP is to abandon the goal of diagonalizing  $\Lambda_j^i$  and be satisfied with a nearly block-diagonal one. A programmable recursive refinement procedure is provided to successively weaken the fast-slow couplings.

Pragmatically, the extraction of physical insights from the CSP data is advantageous only if the CSP data, such as the participation index and the



importance index, changes less rapidly with time than the solution  $\mathbf{y}(t)$ . In problems involving chemical reactions, the basic chemical process is usually described by a reaction rate  $F^r$  and a *constant* stoichiometric vector  $\mathbf{s}_r$ . Whatever simplifications which are available can usually be attributed to some reactions being much faster than others and had now spent themselves. As a consequence, good decoupling basis vectors in chemical kinetics are most likely to be weakly time-dependent, because the relevant chemically meaningful stoichiometric vectors of the fast reactions are time-independent. In the example studied in §3.3, the information extracted from the CSP data hardly change with time at all, because the “mechanism” of the problem did not change.

The CSP algorithm depend on the fast modes to become exhausted, which translates into assuming that the fast eigen-values of  $\mathbf{J}$  are “essentially real” and negative. Theoretically, if a highly oscillatory fast mode does not damp out (*i.e.* a Wentzel, Kramers and Brillouin (WKB) type problem), CSP will only be able to identify this mode, but will not be able to provide an algorithm to handle the evolution of  $\mathbf{y}$  in the next larger time scale. The extension of CSP to WKB type problems remains to be explored.

CSP can be used, in principle, on problems which have a large number of modes but only moderate amount of time scale separation (*i.e.* the ratio,  $(\tau(M+1)/\tau(M))$ , is only moderately large), provided that only moderate accuracy is desired. It thrives on large time scale separations, and performs best when the separations are “asymptotically large.”

## 9 Concluding Remarks

A computer code, called CSP91 and programmed by Dr. Dimitris Goussis, has implemented the CSP algorithm, and is available on request. The code can be used either as a diagnostics subroutine, or as a stiff ODE solver. It has been used to demonstrate in a number of test problems (Lam *et. al.*, 1989; Goussis *et. al.* 1990; Goussis and Lam, 1992) that numerical solutions generated by the CSP-derived simplified models are in quantitative agreement with that of the corresponding full models in accordance to the accuracy thresholds specified. Different simplified models are generated for different user-specified  $\mathbf{y}_{error}$ . The CSP-derived insights, such as which fast reactions are in partial-equilibrium with each other (through the participation indices),

which reactions are rate-controlling (through the importance indices), which species can be considered as radicals in the CSP context (through the radical pointers) and how they can be solved for from the equations of state (through the radical correction), have been thoroughly tested and verified. In most cases, the CSP-derived insights are consistent with the expectations of competent chemical kineticists knowledgeable in the reaction system under study. For the few cases when the CSP-derived insights appeared surprising at first sight, they all eventually became obvious after further reflections.

## References

- Aiken, R. C. (1985). *Stiff Computation*, Oxford University Press.
- Bilger, R. W., M. B. Esler, and Starner, S. H. (1991). In *Reduced Kinetic Mechanisms and Asymptotic Approximations for Methane-Air Flames*, Chapter 5: "On Reduced Mechanisms for Methane-Air Combustion," Lecture Notes in Physics 384, M. Smooke, Ed., Springer-Verlag.
- Bilger, R. W., Starner, S. H. and Kee, R. J. (1990). "On the Reduced Mechanisms for Methane-Air Combustion in Non-Premixed Flames, *Combust. Flame* 80, p. 135.
- Chelliah, H. K. and Williams, F. A. (1990). "Aspects of the Structure and Extinction of Diffusion Flames in Methane-Oxygen-Nitrogen Systems," *Combust. Flame*, 80, pp. 17-48.
- Goussis, D. A., S. H. Lam and Gnoffo, P.A. (1990). "Reduced and Simplified Chemical Kinetics for Air Dissociation Using Computational Singular Perturbation", AIAA 28th Aerospace Sciences Meeting, (AIAA 90-0644), Reno, Nevada, January 9-12.
- Goussis, D. A. and Lam, S. H. (1992). "A Study of Homogeneous Methanol Oxidation Kinetics Using CSP," *Proceedings of the 24th International Symposium on Combustion*, University of Sydney, Sydney, Australia, July 5-10.
- Lam, S. H. (1985). "Singular Perturbation for Stiff Equations Using Numerical Methods", in *Recent Advances in the Aerospace Sciences*, Corrado Casci, Ed., Plenum Press, New York and London, pp.3-20.
- Lam, S. H. and Goussis, D. A. (1988a). "Basic Theory and Demonstrations of Computational Singular Perturbation for Stiff Equations", *12th IMACS*

*World Congress on Scientific Computation*, Paris, France, July 18-22, 1988; IMACS Transactions on Scientific Computing '88, Numerical and Applied Mathematics, C. Brezinski, Ed., J. C. Baltzer A. G. Scientific Publishing Co., pp. 487-492.

Lam, S. H. and Goussis, D. A. (1988b). "Understanding Complex Chemical Kinetics With Computational Singular Perturbation", *Proceedings of the 22nd International Symposium on Combustion*, pp. 931-941, University of Washington, Seattle, Washington, August 14-19.

Lam, S. H., Goussis, D. A., and Konopka, D. (1989). "Time-Resolved Simplified Chemical Kinetics Modeling Using Computational Singular Perturbation", AIAA 27th Aerospace Sciences Meeting, (AIAA 89-0575), Reno, Nevada, January 9-12.

Lam, S. H. and Goussis, D. A. (1991a). In *Reduced Kinetic Mechanisms and Asymptotic Approximations for Methane-Air Flames*, Chapter 10: "Conventional Asymptotics and Computational Singular Perturbation for Simplified Kinetics Modeling," Lecture Notes in Physics 384, M. Smooke, Ed., Springer-Verlag.

Lam, S. H. and Goussis, D. A. (1991b). "Identification of Intermediaries and Fast Reactions in Complex Chemical Mechanisms Using CSP," presented at the 4th International Conf. Numerical Combustion, St. Petersburg Beach, Florida, December 2-4.

Maas, U. and Pope, S. B. (1992). "Simplifying Chemical Kinetics: Intrinsic Low-Dimensional Manifolds in Composition Space," *Combust. Flame*, **88**, pp. 239-264.

Noble, B. and Daniel, J. W. (1988). *Applied Linear Algebra*, Third Edition, Prentice Hall, Inc.

Peters, N. (1985). "Numerical Simulation of Combustion Phenomena", R. Glowinski, B. Larrourou, and R. Temam, Eds., Lecture Notes in Physics 241, pp. 90-109, Springer-Verlag, New York.

Peters, N. (1991). In *Reduced Kinetic Mechanisms and Asymptotic Approximations for Methane-Air Flames*, Chapter 3: "Reduced Mechanisms," Lecture Notes in Physics 384, M. Smooke, Ed., Springer-Verlag.

Peters, N. and Williams F. A. (1987). "The Asymptotic Structure of Stoichiometric Methane-Air Flames", *Combust. Flame*, **68**, pp. 185-207.

Trevino, C. and Solorio, F. (1991). "Asymptotic Analysis of the High Temperature Ignition of  $CO/H_2/O_2$  Mixtures," *Combust. Flame*, **86**, pp. 285-295.

Trevino, C. (1991). "Ignition Phenomena in  $H_2-O_2$  Mixtures," in *Dynamics of Deflagration and Reactive Systems and Flames*, A. L. Kuhl et. al., Ed., Progress in Aeronautics and Astronautics, AIAA.

Williams, F.A. (1985). *Combustion Theory, The Fundamental Theory of Chemically Reacting Systems*, 2nd edition, Benjamin/Cummings Publ. Co., Menlo Park, Ca.

Yetter, R. A., Dryer, F. L. and Rabitz, H. (1991). "A Comprehensive Reaction Mechanism of Carbon Monoxide/Hydrogen/Oxygen Kinetics," *Combust. Sci. Tech.*, **79**, pp. 97-128.

## **Appendix II**

### **A Study of Homogeneous Methanol Oxidation Kinetics Using CSP**

24th Symposium (International) on Combustion, The Combustion  
Institute, Pittsburgh, PA, pp.113-120, 1992.

## A STUDY OF HOMOGENEOUS METHANOL OXIDATION KINETICS USING CSP

D. A. Goussis and S. H. Lam

Princeton University, Princeton, NJ 08544

## Abstract

The homogeneous oxidation of methanol in air at constant pressure is examined using data generated by the method of *computational singular perturbation* (CSP). At any moment in time, the number of exhausted fast modes and the radicals (sometimes called the intermediaries) are computationally identified. The *participation index*, which quantifies the participation of any elementary reaction to an *equations of state* of the radicals, along with the *importance index*, which quantifies the importance of any elementary reaction to a particular species of interest, are computed and used to assess the sensitivities of the solution to the reaction rate constants. Every elementary reaction is classified so that it either belongs to the *equilibrated set* which contains fast reactions already equilibrated among themselves, and/or the *rate-controlling set* which contains reactions controlling the current rate of activities, or neither of the above sets – in which case it is superfluous. A number of numerical experiments were performed to verify the assessments: (a) the relative effectiveness of the reaction rate constants of two reactions (#16, #160) in breaking up the fuel indicated by the importance index is verified, (b) that fuel breakup in an early time period can actually be slowed down by increasing the reaction rate constants of certain fuel breakup reactions (#156, #159) is verified. Numerical experiments also show that species identified as radicals respond instantly to sudden changes in reaction rates, while the non-radicals respond more smoothly. The overall response of the unknowns to perturbations is always consistent with the CSP-derived *effective stoichiometric coefficients*. In addition, a *minimum set* of species is constructed with the help of the CSP data. This minimum set, which trims the original full set of 30 species to 15 species, generates numerical solutions in excellent agreement with solutions obtained with the full set.

## 1. Introduction.

The present paper studies the constant pressure oxidation of methanol in air. The full kinetics mechanism, taken from Egolfopoulos, Du and Law<sup>1</sup> [EDL], consists of 30 species and 173 reversible elementary reactions. A partial list of the elementary reactions is given in Appendix I. The case of a fuel-lean (equivalence ratio=0.6) mixture at 1 atmosphere will be considered. The initial state of the system is taken to be:  $T(0) = 1027^\circ\text{K}$ ,  $Y[\text{CH}_3\text{OH}](0) = 0.00779$ ,  $Y[\text{O}_2](0) = 0.01980$ ,  $Y[\text{N}_2](0) = 0.9724$ , where  $T$  is temperature and  $Y$  is mass fraction. The calculation is performed in a Chemkin environment<sup>2</sup>, and the resulting numerical solution is analyzed using the

data generated by the method of *computational singular perturbation (CSP)* developed by the authors<sup>3,4,5</sup>.

Figs. 1a and 1b show the time evolution of four species; similar plots for all the other species and the temperature are readily available. The oxidation of CH<sub>3</sub>OH can be described as a four-stage process. The first stage, 0.00 seconds < t < 0.05 seconds, is an incubation period in which certain radicals are created. The breakup of the fuel occurs in the second stage, 0.050 seconds < t < 0.079 seconds. The third stage, 0.079 < t < 0.081, consists of the very rapid conversion of CO to CO<sub>2</sub>. The conversion of the remaining CO to CO<sub>2</sub> takes place in the fourth stage, 0.081 < t < 0.130, with progressively slower rates. The integration of the kinetics equations is straightforwardly performed by a CSP ODE solver which, in addition to generating solutions of guaranteed user-specified accuracy, also generates a set of CSP data. Each time interval between markers shown in Figs. 1a,b covers 24 integration time steps selected by the CSP code.

## 2. Preliminary Discussions

The conventional derivation of a simplified model requires that the "radicals" and fast reactions in the reaction system be somehow identified, and the quasi-steady and partial-equilibrium approximations be systematically<sup>6,7,8,9</sup> applied. Considerable intuition, experience and mathematical skills are required. The simplified model so obtained is highly valued because it identifies the rate-controlling elementary reactions, and can be used to provide or interpret the sensitivity information<sup>10,11,12</sup> of the reaction system. The CSP method performs the above tasks routinely using a programmable computational algorithm, and can generate time-resolved simplified models without the need of intuition and experience. A brief summary of the CSP method is given in Appendix II.

## 3. The Identification of Radicals

Including temperature, the system of ODEs of the [EDL] full mechanism consists of 31 unknowns and 173 reversible elementary reactions. Let  $y = [Y^1, Y^2, \dots, Y^N]^T$  be a column vector of the  $N = 31$  unknowns. Let  $F_+^k(y) \geq 0$  and  $F_-^k(y) \geq 0$  be the forward and backward reaction rates of the  $k$ -th elementary reactions, where  $k=1, 2, \dots, R$  with  $R=173$ . In general, the governing equations can be written in the following compact form:

$$\frac{dy}{dt} = g(y) = s_k \{F_+^k - F_-^k\}, \quad (2.1)$$

where  $s_k$  is called the *stoichiometric vector* of the  $k$ -th elementary reaction, and the summation convention is used. Since this is a 31-dimensional system, the solution is expected to have 31 "modes." These modes are ordered by CSP according to their speed: mode #1 being the fastest and mode #26 being the slowest. Modes #27 to #31 are constants and do not evolve with time; they represent the conservation of energy, the conservation of C, H, and O atoms and the inertness of  $N_2$ . In addition, CSP computationally determines  $M$ , the number of *exhausted fast modes* (see Appendix II). Fig. 2 shows  $M$  vs. time. Each of the exhausted fast modes is associated by CSP with either a quasi-steady approximation (for a certain radical species) or a partial-equilibrium approximation (for a certain set of fast reactions). In the present paper, we shall call a species a *radical* when it can accurately be computed in terms of the other "major species" from certain approximate "equations of state" derived by CSP. More will be said on this in §4 later. The identification of these radicals was achieved by the use of  $Q(m; i)$ , the "radical pointer" of each of the  $m$  exhausted modes, as described in Appendix II.

The following information is obtained from the CSP data for each of the four stages:

First Stage ( $0.00 < t < 0.05$  seconds).  $M = 14$ . The following 14 species are identified as radicals:  $CH_3$ ,  $C_2H_5$ ,  $CH_3CO$ ,  $HCO$ ,  $H$ ,  $CH_2$ ,  $C_2H_3$ ,  $CH_2OH$ ,  $HCCO$ ,  $O$ ,  $CH$ ,  $C_2H$ ,  $CH_3O$ ,  $OH$ .

Second Stage ( $0.050 < t < 0.079$  seconds).  $M = 15$ .  $HO_2$  joins the above, making a total of 15 radicals. The breakup of the fuel is in full swing.

Third Stage ( $0.079 < t < 0.081$  seconds).  $M = 12$ . This is a most active period in which things happen very rapidly. Three exhausted modes becomes alive again, and  $CH_3$ ,  $H$  and  $O$  are temporarily removed from the list of radicals.

Fourth Stage ( $0.081 < t < 0.130$  seconds).  $M = 15-24$ . After the frenzy activities in the third stage,  $CH_3$ ,  $H$  and  $O$  rejoins the list of radicals. As the fourth stage progresses,  $M$  increases from 15 to 24, mostly as the results of extinction of the carbon related species ( $CO$  and  $CO_2$  excluded). The remaining non-carbon related radicals in this late period are  $O$ ,  $H$ ,  $OH$ ,  $HO_2$  and  $H_2O_2$ .

#### 4. The Simplified Model at $t=0.0345$

We shall demonstrate in some detail the procedures for extracting information about the reaction system using the CSP data in one typical moment in time. At  $t = 0.0345$ , when the fuel is breaking up and  $HO_2$  is not yet a radical but is about to peak, CSP determined  $M = 14$ , and generated 14 approximate "equations of state":



$$f^m(y) \approx 0, \quad m = 1, \dots, 14. \quad (4.1)$$

Each of these equations of state can be physically interpreted either as a quasi-steady approximation or a partial-equilibrium approximation. Samples of these 14 equations of state, suitably normalized, are displayed below:

Exhausted Mode #1 [CH<sub>3</sub>]:

$$\begin{aligned} F_-^{29} &\approx F_+^{33} + F_+^{32} + F_+^{163} + \dots, \\ 0.50 &\approx 0.43 + 0.05 + 0.01 + \dots, \\ &\dots \end{aligned} \quad (4.2a)$$

Exhausted Mode #5 [H]:

$$\begin{aligned} F_+^{43} + F_+^{53} + F_+^3 &\approx F_+^{156} + F_+^{12} + F_+^{38} + F_+^{157} + F_+^1 + F_+^{11} + F_+^9 + \dots, \\ 0.35 + 0.14 + 0.02 &\approx 0.23 + 0.08 + 0.08 + 0.06 + 0.02 + 0.02 + 0.02 + \dots, \\ &\dots \end{aligned} \quad (4.2b)$$

Exhausted Mode #13 [CH<sub>3</sub>O]:

$$\begin{aligned} F_+^{160} + F_+^{157} &\approx F_+^{43} + \dots, \\ 0.42 + 0.08 &\approx 0.48 + \dots, \\ &\dots \end{aligned} \quad (4.2c)$$

Each exhausted mode is identified by the radical pointer  $Q(m; i)$  described in Appendix II with a specific species which shall be referred to as a *radical*. The left and right hand sides of (4.2a,b,c) are the rates of production and consumption of the identified radical. The terms on each side are ordered in descending order of magnitude; sufficient terms are kept so that the total contribution of the omitted terms is below a user-specified threshold. The numbers displayed below each term is the *participation index*,  $P_k^m$ , which is defined in Appendix II and measures the significance of the  $k$ -th reaction to the  $m$ -th exhausted fast mode.

In addition, CSP derives the following simplified model:

$$\frac{dy}{dt} \approx c_k \{F_+^k - F_-^k\}, \quad (4.3)$$

where  $c_k$  is called the *effective stoichiometric vector* of the  $k$ -th reaction. Mathematically, it is the projection of the original stoichiometric vector  $s_k$  in the currently active *slow subspace*. Samples of these 31 equations are displayed below:

$$\frac{d[\text{CH}_4]}{dt} = c_{16}^{17} F_+^{16} + c_{160}^{17} F_+^{160} + c_{29}^{17} F_-^{29} + c_{43}^{17} F_+^{43} + c_{156}^{17} F_+^{156} + c_{33}^{17} F_+^{33} + c_{159}^{17} F_+^{159}$$

$$+ \dots, \quad [\text{CH}_4] = Y^{17}, \quad (4.4a)$$

$$\frac{d[\text{H}]}{dt} = c_{16}^7 F_+^{16} + c_{15}^7 F_+^{15} + c_{162}^7 F_+^{162} + \dots, \quad [\text{H}] = Y^7, \quad (4.4b)$$

$$\begin{aligned} \frac{d[\text{CH}_3\text{OH}]}{dt} = & c_{16}^{15} F_+^{16} + c_{160}^{15} F_+^{160} + c_{40}^{15} F_+^{40} + c_{162}^{15} F_+^{162} + c_{57}^{15} F_+^{57} + c_{53}^{15} F_+^{53} \\ & - 0.40 \quad - 0.16 \quad + 0.12 \quad - 0.05 \quad + 0.05 \quad + 0.05 \\ & + \dots, \quad [\text{CH}_3\text{OH}] = Y^{15}, \end{aligned} \quad (4.4c)$$

where the coefficients  $c_k^i$  (the  $i$ -th element of  $c_k$ ) are provided by CSP numerically. The numbers displayed below each term in (4.4c) is the *importance index*,  $I_k^{15}$ , a measure of the significance of the  $k$ -th reaction to the simplified equation for  $\text{CH}_3\text{OH}$ . The definition of  $I_k^i$  is given in Appendix II. Again, the terms on the right hand side are ordered in descending magnitude; sufficient terms are kept so that the total of the omitted terms is below a user-specified threshold. Note that the solution of these 31 equations *automatically* satisfies the 14 approximate equations of state given symbolically by (4.1) and explicitly by (4.2). One may freely replace the differential equation for any radical, such as (4.4b), by its equation of state, in this case (4.2b).

It is interesting to compare the CSP derived simplified model equations with the original equations. For  $[\text{CH}_3\text{OH}]$ , the original equation is:

$$\left( \frac{d[\text{CH}_3\text{OH}]}{dt} \right)_{\text{original}} \approx - \frac{32}{\rho} \{ F_+^{159} + F_+^{160} + F_+^{156} + F_+^{162} + F_+^{157} + \dots \}, \quad (4.5a)$$

where  $\rho$  is total mass density. Using the CSP-computed numerical values for  $C_k^{15}$ , the simplified equation for  $[\text{CH}_3\text{OH}]$  is:

$$\begin{aligned} \left( \frac{d[\text{CH}_3\text{OH}]}{dt} \right)_{\text{CSP}} \approx & - \frac{32}{\rho} \{ 2.25 F_+^{16} + 1.19 F_+^{160} - 0.75 F_+^{40} + F_+^{162} - 0.34 F_+^{57} + 0.94 F_+^{53} \\ & + \dots \}. \end{aligned} \quad (4.5b)$$

The terms in (4.5a,b) are ordered in descending magnitude. In contrast to (4.5a) where each term involves methanol as a participant in a reaction, only reactions #160 and #162 in (4.5b) directly involve methanol. Similar observation can be made for all the simplified equations. For example, none of the seven reactions listed in the CSP-derived (4.4a) for  $[\text{CH}_4]$  involves  $\text{CH}_4$ . Theoretically, the difference between the right hand side of the original and the CSP-derived simplified equations is some linear combinations of the equations of state given symbolically by (4.1) and explicitly by (4.2). Even though the CSP-derived simplified equations frequently do not make chemical sense at first glance, our experience is that they usually make sense upon further

reflections. Computationally, solutions obtained from the CSP-derived simplified equations and from the full equations agree within user-specified bounds.

Similar information can be obtained for any moment in time.

### 5. The Importance Index

The importance index  $I_k^i$  defined in Appendix II measures the importance of the  $k$ -th reaction to the  $i$ -th unknown. Figs. 3a and 3b show  $I_k^{15}$ , the importance index for  $\text{CH}_3\text{OH}$ , for reactions which do and do not involve  $\text{CH}_3\text{OH}$ , respectively. These two graphs provide concise information on the rate-controlling reactions for the breakup of  $\text{CH}_3\text{OH}$ . By inspection, Fig. 3a,b show that reaction #16 is the most effective reaction in both the first and the second stages, even though it does not directly involve  $\text{CH}_3\text{OH}$ . It is seen to be somewhat more effective than reactions #160 and #162 which do. A numerical experiment was performed by increasing the rate constants for reactions #16 and #160 by a factor of 2.5 in the first stage. The computed time histories of  $\text{CH}_3\text{OH}$  confirmed the above qualitative prediction.

In addition, Fig. 3a shows that reactions #156 and #159, which chemically consume  $\text{CH}_3\text{OH}$ , have positive importance indices in the  $0.00 \leq t \leq 0.03$  period:  $I_{156}^{15} > 0$  and  $I_{159}^{15} > 0$ . In other words, they effectively contribute positive terms in the first stage to the right hand side of (4.4c) – a somewhat counter-intuitive prediction. Another numerical experiment was performed in which the rate constants for reactions #156 and #159 were simultaneously doubled. The resulting data shows that the breakup of  $\text{CH}_3\text{OH}$  was indeed slowed and delayed in the first stage, again confirming the CSP expectation. In the third stage, however, faster #156 and #159 do favor the breakup of  $\text{CH}_3\text{OH}$ , as indicated also by Fig. 3a.

### 6. Classification of Reactions

The left hand side of (4.1) consists of positive and negative terms which nearly cancel each other. Separating the positive and negative terms and placing them across an equal sign as is done in (4.2) for each of the exhausted modes, we can pick out reactions which participate most significantly on each side using the participation index,  $P_k^m$ , defined and described in Appendix II. We shall call the total collection of such reactions the *equilibrated set*. Loosely speaking, these are the fast reactions which have equilibrated among themselves. At  $t = 0.0345$ , the equilibrated set consists of: forward 1, 3, 9, 11-14, 16, 30, 32, 33, 35, 38-41, 43, 53, 57, 65, 67, 71-74, 78, 84, 86, 94, 98, 101, 109, 110, 116, 120, 123, 128, 132, 141-143, and backward 29, 113, 118, 142, 147, 149.

We can pick out, for each unknown, reactions which contribute most significantly to the right hand side of (4.3) using the importance index,  $I_k^i$ . We shall call these the *rate-controlling set*. Loosely speaking, these are the slower reactions currently driving the system. At  $t = 0.0345$ , the rate-controlling set consists of: forward 12, 14-16, 33, 38, 40, 41, 43, 53, 57, 58, 60, 62, 101, 109, 110, 127, 156, 157, 159, 160, 162, and backward 29, 102, 127, 136. Note that these two sets are not totally distinct; some reactions (*e.g.* 12, 14, 16, *etc.*) belong to both sets. A reaction which belongs to neither set is obviously not important to the system and is therefore superfluous at that moment in time.

The reactions which only belong to the equilibrated set define via (4.1) the so-called *slow subspace* which may be visualized as a  $(N-M)$ -dimensional "surface" on which the  $N$ -dimensional solution point  $y(t)$  moves. Changing the rate constants in the equilibrated set changes the surface, but does not change the speed of the motion. The reactions which only belong to the rate-controlling set control the speed of the motion of  $y(t)$ , but do not affect the surface on which it moves. The reactions which belong to both sets affect both. Numerical experiments were performed by perturbing the reaction rate of reactions #15 in a step-function manner for  $t \geq 0.0345$ . Since #15 belongs only to the rate-controlling set, the response of  $y(t)$  to this abrupt perturbation is smooth and agree qualitatively with the CSP expectations. additional numerical experiments were performed by perturbing the reaction rate of reaction #160 which belongs to both sets. The response of  $y(t)$  is again in qualitative agreement with the CSP expectations: some radicals respond discontinuously, all major species respond smoothly. Such information can be very useful in reaction-path analysis.

## 7. The Minimum Set of Species

Normally, one is usually interested only in the time history of a few species in a reaction system. Using the data generated by CSP, it is straight-forward to use the CSP data to identify *the minimum set* of unknowns (species) which includes an user-specified species of interest. The following minimum set which includes  $\text{CH}_3\text{OH}$  is obtained for the time interval studied:  $\text{CH}_3\text{OH}$ ,  $\text{CH}_2\text{O}$ ,  $\text{H}$ ,  $\text{H}_2\text{O}_2$ ,  $\text{CH}_3\text{O}$ ,  $\text{CH}_3$ ,  $\text{H}_2$ ,  $\text{HO}_2$ ,  $\text{CH}_2\text{OH}$ ,  $\text{CO}$ ,  $\text{O}$ ,  $\text{H}_2\text{O}$ ,  $\text{HCO}$ ,  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{OH}$ . The solution of this minimum set of 16 species (plus temperature) system is in excellent agreement with the solution computed from the full reaction system. Comparison of results obtained for  $\text{CO}$  and  $\text{H}$  are shown in Fig. 1b.

## 8. Conclusions

Neither of the authors are knowledgeable about chemical kinetics in general, and about methanol oxidation in particular. The above information are presumed by us to be informative, and are obtained routinely using the CSP data generated by the CSP code. Because of limitation of space, only part of the available information is included here<sup>13</sup>. The method is clearly useful for the study of massively complex systems when intuition and experience are lacking and conventional analysis is untenable.

## Appendix I

## Selected Elementary Reactions From Full Kinetics Mechanism of [EDL]

- |   |  |
|---|--|
| (1) $\text{H} + \text{O}_2 = \text{O} + \text{OH}$                                | (84) $\text{C}_2\text{H}_6 + \text{H} = \text{C}_2\text{H}_5 + \text{H}_2$               |
| (3) $\text{OH} + \text{H}_2 = \text{H} + \text{H}_2\text{O}$                      | (86) $\text{C}_2\text{H}_6 + \text{OH} = \text{C}_2\text{H}_5 + \text{H}_2\text{O}$      |
| (4) $\text{OH} + \text{OH} = \text{O} + \text{H}_2\text{O}$                       | (94) $\text{C}_2\text{H}_5 + \text{O}_2 = \text{C}_2\text{H}_4 + \text{HO}_2$            |
| (9) $\text{H} + \text{O}_2 + \text{M} = \text{HO}_2 + \text{M}$                   | (98) $\text{C}_2\text{H}_4 + \text{H} = \text{C}_2\text{H}_3 + \text{H}_2$               |
| (11) $\text{HO}_2 + \text{H} = \text{O}_2 + \text{H}_2$                           | (101) $\text{C}_2\text{H}_4 + \text{OH} = \text{C}_2\text{H}_3 + \text{H}_2\text{O}$     |
| (12) $\text{HO}_2 + \text{H} = \text{OH} + \text{OH}$                             | (102) $\text{C}_2\text{H}_4 + \text{OH} = \text{CH}_3 + \text{CH}_2\text{O}$             |
| (13) $\text{HO}_2 + \text{O} = \text{OH} + \text{O}_2$                            | (109) $\text{C}_2\text{H}_3 + \text{O}_2 = \text{C}_2\text{H}_2 + \text{HO}_2$           |
| (14) $\text{HO}_2 + \text{OH} = \text{H}_2\text{O} + \text{O}_2$                  | (110) $\text{C}_2\text{H}_3 + \text{O}_2 = \text{CH}_2\text{O} + \text{HCO}$             |
| (15) $\text{HO}_2 + \text{HO}_2 = \text{H}_2\text{O}_2 + \text{O}_2$              | (113) $\text{C}_2\text{H}_2 + \text{H} = \text{C}_2\text{H} + \text{H}_2$                |
| (16) $\text{H}_2\text{O}_2 + \text{M} = 2\text{OH} + \text{M}$                    | (116) $\text{C}_2\text{H}_2 + \text{OH} = \text{C}_2\text{H} + \text{H}_2\text{O}$       |
| (29) $\text{CH}_3 + \text{OH} = \text{CH}_3\text{O} + \text{H}$                   | (120) $\text{C}_2\text{H} + \text{O}_2 = \text{CO} + \text{HCO}$                         |
| (30) $\text{CH}_3 + \text{OH} = \text{CH}_2 + \text{H}_2\text{O}$                 | (123) $\text{CH}_2\text{CO} + \text{H} = \text{HCCO} + \text{H}_2$                       |
| (32) $\text{CH}_3 + \text{O}_2 = \text{CH}_2\text{O} + \text{O}$                  | (127) $\text{CH}_2\text{CO} + \text{OH} = \text{CH}_2\text{O} + \text{HCO}$              |
| (33) $\text{CH}_3 + \text{HO}_2 = \text{CH}_3\text{O} + \text{OH}$                | (128) $\text{CH}_2\text{CO} + \text{OH} = \text{HCCO} + \text{H}_2\text{O}$              |
| (35) $2\text{CH}_3 = \text{C}_2\text{H}_5 + \text{H}$                             | (132) $\text{HCCO} + \text{O}_2 = 2\text{CO} + \text{OH}$                                |
| (36) $2\text{CH}_3 (+\text{M}) = \text{C}_2\text{H}_6 (+\text{M})$                | (136) $\text{CH}_3\text{HCO} = \text{CH}_3 + \text{HCO}$                                 |
| (38) $\text{CH}_2\text{O} + \text{H} = \text{HCO} + \text{H}_2$                   | (142) $\text{CH}_3\text{CO} + \text{M} = \text{CH}_3 + \text{CO} + \text{M}$             |
| (39) $\text{CH}_2\text{O} + \text{O} = \text{HCO} + \text{OH}$                    | (143) $\text{CH}_3\text{CO} + \text{H} = \text{CH}_3 + \text{HCO}$                       |
| (40) $\text{CH}_2\text{O} + \text{OH} = \text{HCO} + \text{H}_2\text{O}$          | (147) $\text{CH}_3\text{CO} + \text{H}_2 = \text{CH}_3\text{HCO} + \text{H}$             |
| (41) $\text{CH}_2\text{O} + \text{HO}_2 = \text{HCO} + \text{H}_2\text{O}_2$      | (154) $\text{CH}_3\text{OH} (+\text{M}) = \text{CH}_3 + \text{OH} (+\text{M})$           |
| (43) $\text{CH}_3\text{O} + \text{M} = \text{CH}_2\text{O} + \text{H} + \text{M}$ | (155) $\text{CH}_3\text{OH} (+\text{M}) = \text{CH}_2\text{OH} + \text{H} (+\text{M})$   |
| (53) $\text{HCO} + \text{M} = \text{CO} + \text{H} + \text{M}$                    | (156) $\text{CH}_3\text{OH} + \text{H} = \text{CH}_2\text{OH} + \text{H}_2$              |
| (57) $\text{HCO} + \text{O}_2 = \text{CO} + \text{HO}_2$                          | (157) $\text{CH}_3\text{OH} + \text{H} = \text{CH}_3\text{O} + \text{H}_2$               |
| (58) $\text{HCO} + \text{HO}_2 = \text{CO}_2 + \text{OH} + \text{H}$              | (158) $\text{CH}_3\text{OH} + \text{O} = \text{CH}_2\text{OH} + \text{OH}$               |
| (60) $\text{CO} + \text{OH} = \text{CO}_2 + \text{H}$                             | (159) $\text{CH}_3\text{OH} + \text{OH} = \text{CH}_2\text{OH} + \text{H}_2\text{O}$     |
| (62) $\text{CO} + \text{HO}_2 = \text{CO}_2 + \text{OH}$                          | (160) $\text{CH}_3\text{OH} + \text{OH} = \text{CH}_3\text{O} + \text{H}_2\text{O}$      |
| (65) $\text{CH} + \text{O}_2 = \text{HCO} + \text{O}$                             | (161) $\text{CH}_3\text{OH} + \text{O}_2 = \text{CH}_2\text{OH} + \text{HO}_2$           |
| (67) $\text{CH}_2 + \text{H} = \text{CH} + \text{H}_2$                            | (162) $\text{CH}_3\text{OH} + \text{HO}_2 = \text{CH}_2\text{OH} + \text{H}_2\text{O}_2$ |
| (71) $\text{CH}_2 + \text{OH} = \text{CH} + \text{H}_2\text{O}$                   | (163) $\text{CH}_3\text{OH} + \text{CH}_3 = \text{CH}_2\text{OH} + \text{CH}_4$          |
| (72) $\text{CH}_2 + \text{O}_2 = \text{CO}_2 + \text{H} + \text{H}$               | (164) $\text{CH}_3\text{OH} + \text{CH}_3 = \text{CH}_3\text{O} + \text{CH}_4$           |
| (73) $\text{CH}_2 + \text{O}_2 = \text{CH}_2\text{O} + \text{O}$                  | (167) $\text{CH}_2\text{OH} + \text{O}_2 = \text{CH}_2\text{O} + \text{HO}_2$            |
| (74) $\text{CH}_2 + \text{O}_2 = \text{CO}_2 + \text{H}_2$                        | (170) $\text{CH}_2\text{OH} + \text{CH}_3 = \text{C}_2\text{H}_5 + \text{OH}$            |
| (78) $\text{CH}_2 + \text{H}_2\text{O}_2 = \text{CH}_3\text{O} + \text{OH}$       |  |

## Appendix II

### A Summary of CSP Concepts

#### A1 Basic CSP Concepts and Data

The basic CSP idea is to split the N-dimensional space of the vector  $\mathbf{g}$  into two subspaces, a fast and a slow subspace:

$$\mathbf{g} = \mathbf{g}^{\text{fast}} + \mathbf{g}^{\text{slow}}, \quad (\text{A1.1})$$

where  $\mathbf{g}^{\text{fast}}$  is spanned by a set of M linearly independent column basis vectors  $\mathbf{a}_m$ , ( $m=1, 2, \dots, M$ ). CSP provides an algorithm<sup>5</sup> to determine M and to compute for this set of  $\mathbf{a}_m$  along the trajectory of the solution  $\mathbf{y}(t)$ , together with a set of row vectors  $\mathbf{b}^m$  which is ortho-normal to  $\mathbf{a}_m$ :  $\mathbf{b}^m \cdot \mathbf{a}_n = \delta_n^m$ ,  $m, n = 1, 2, \dots, M$ .

The time-resolved values of M, the basis vectors  $\mathbf{a}_m$  and  $\mathbf{b}^m$  appropriately ordered in ascending time scales, are the basic CSP data.

#### A.2 Using the Basis Vectors

The fast subspace, being M-dimensional, contains M fast reaction modes, or simply modes. For chemical kinetics problems, these modes are usually decaying modes; *i.e.* they tend to become exhausted. When  $\mathbf{g}^{\text{fast}}$  falls below some user-specified threshold for  $t \geq t_M$ , we have:

$$\mathbf{g}^{\text{fast}} \approx 0, \quad (\text{A2.1})$$

which yields M algebraic relations between the elements of  $\mathbf{y}$ . In other words, M *equations of state*, usually derived analytically using conventional singular perturbation technique, are directly obtained from (A2.1). Another consequence is that an approximate time evolution equation for  $\mathbf{y}$  is obtained for  $t \geq t_M$ :

$$\frac{d\mathbf{y}}{dt} \approx \mathbf{g}^{\text{slow}}, \quad (\text{A2.2})$$

which is the desired simplified model of the reaction system. CSP guarantees<sup>5</sup> that solutions of (A2.2) satisfying (A2.1) at  $t = t_M$  will satisfy (A2.1) for  $t \geq t_M$ , under fairly general conditions.

With M and both  $\mathbf{a}_m$  and  $\mathbf{b}^m$  available, we can express  $\mathbf{g}^{\text{fast}}$  in terms of them:

$$\mathbf{g}^{\text{fast}} = \mathbf{a}_m \mathbf{b}^m \cdot \mathbf{g} = \mathbf{a}_m \mathbf{f}^m, \quad (\text{A2.3})$$

where  $\mathbf{f}^m = \mathbf{b}^m \cdot \mathbf{g} = \mathbf{B}_k^m (\mathbf{F}_+^k - \mathbf{F}_-^k)$ ,  $\mathbf{B}_k^m = \mathbf{b}^m \cdot \mathbf{s}_k$ . Using (A2.3) in (A1.1) and solving for  $\mathbf{g}^{\text{slow}}$ , we have:

$$\mathbf{g}^{\text{slow}} = \mathbf{c}_k \{F_+^k - F_-^k\}, \quad (\text{A2.4a})$$

$$\mathbf{c}_k = (\mathbf{I} - \mathbf{a}_m \mathbf{b}^m) \cdot \mathbf{S}_k, \quad (\text{A2.4b})$$

where  $\mathbf{c}_k$  is called the *effective stoichiometric vector*, and elements of this column vector,  $c_k^i$ , are called the *effective stoichiometric coefficients* of the  $k$ -th reaction.

### A.3 Participation Index, Importance Index and the Radical Pointer

CSP requires the user to specify  $\Delta y_{\text{error}}$ , the absolute or relative error allowed for each dependent variables. The CSP-derived (A2.2) can be numerically integrated using some non-stiff solver using the CSP-recommended integration step-size,  $\Delta t$ . The error that can be tolerated by  $\mathbf{g}$  per integration step is therefore:  $\delta \mathbf{g} \equiv \Delta y_{\text{error}} / \Delta t$ . Hence the theoretically neglected  $\mathbf{g}^{\text{fast}}$  is numerically negligible during the integration process whenever  $|\mathbf{g}^{\text{fast}}| < \delta \mathbf{g}$ , which serves as the criterion for declaring  $\mathbf{g}^{\text{fast}}$  exhausted. When  $\mathbf{g}^{\text{fast}}$  is declared exhausted, (A2.3) yields:

$$\mathbf{f}^m = \mathbf{B}_k^m \{F_+^k - F_-^k\} \approx 0, \quad m = 1, 2, \dots, M, \quad (\text{A3.1})$$

which are the  $M$  equations of state referred to earlier. In general,  $\mathbf{f}^m \approx 0$  is achieved by near cancellation of the positive and negative terms. Certain terms participate strongly in this balancing act, while others are more or less irrelevant. The *participation index*,  $P_{\pm k}^m$ , is introduced to measure the degree of participation:

$$P_{\pm k}^m \equiv \frac{B_k^m F_{\pm}^{(k)}}{|\mathbf{B}_r^m \{F_+^r + F_-^r\}| + |\mathbf{b}^m \cdot \delta \mathbf{g}|}, \quad (\text{A3.2})$$

where the  $k$  in numerator is not summed and the  $r$  in the denominator is summed over the 173 reactions. As defined, the maximum magnitude of  $P_{\pm k}^m$  is 0.50. In the present study, terms in (A3.1) are ordered in descending magnitude of its  $P_{\pm k}^m$ , and sufficient terms are kept so that the the positive and negative sums are at least 0.48 and -0.48, respectively.

Similarly, not all reactions in (A2.4a) contribute equally to  $\mathbf{g}^{\text{slow}}$ . The *importance index*,  $I_k^i$ , is introduced to assess the degree of importance of the  $k$ -th reaction to the  $i$ -th element of  $\mathbf{y}$ :

$$I_{\pm k}^i = \frac{c_k^i F_{\pm}^{(k)}}{|\mathbf{c}_r^i \{F_+^r + F_-^r\}| + |\delta \mathbf{g}^i|}, \quad (\text{A3.3})$$

the  $k$  and  $r$  indices on the right hand side are treated as before. Again, terms in (A2.4a) are order in descending magnitude of  $I_{\pm k}^i$  so that the sum of  $|I_{\pm k}^i|$  is above some user-specified value (the present paper used 0.9).



In addition, CSP associates with every exhausted mode one or more unknowns which are the "fast" variables responsible for the rapid decay of the mode. The diagonal dimensionless elements of the  $N \times N$  matrix  $\mathbf{a}_m \mathbf{b}^{(m)}$  (no summation on  $m$ ), denoted by  $Q(m; i)$ , are called the *radical pointers* of the  $m$ -th exhausted mode on the  $i$ -th species. *The  $i$ -th species is said to be a fast variable or a radical for the  $m$ -th exhausted mode if  $Q(m; i)$  is not a small number in comparison to unity.* The species with the largest  $Q(m; i)$  is identified as the radical for the  $m$ -th exhausted mode in this paper. If duplication occurs, the next largest pointer is used. The  $M$  relations  $\mathbf{f}^m(\mathbf{y}) \approx 0$  can be used to solve algebraically for these  $M$  radicals in terms of the others. If the "wrong species" are identified as radicals, the solutions of the  $M$  relations are not accurate<sup>14</sup> and can not be trusted.

### Acknowledgements

This work is supported by NASA Langley's Aerothermodynamics Branch, Space Systems Division. The authors acknowledge numerous discussions with Dr. Yetter and Dr. Egolfopoulos during the course of the research.

## Figures

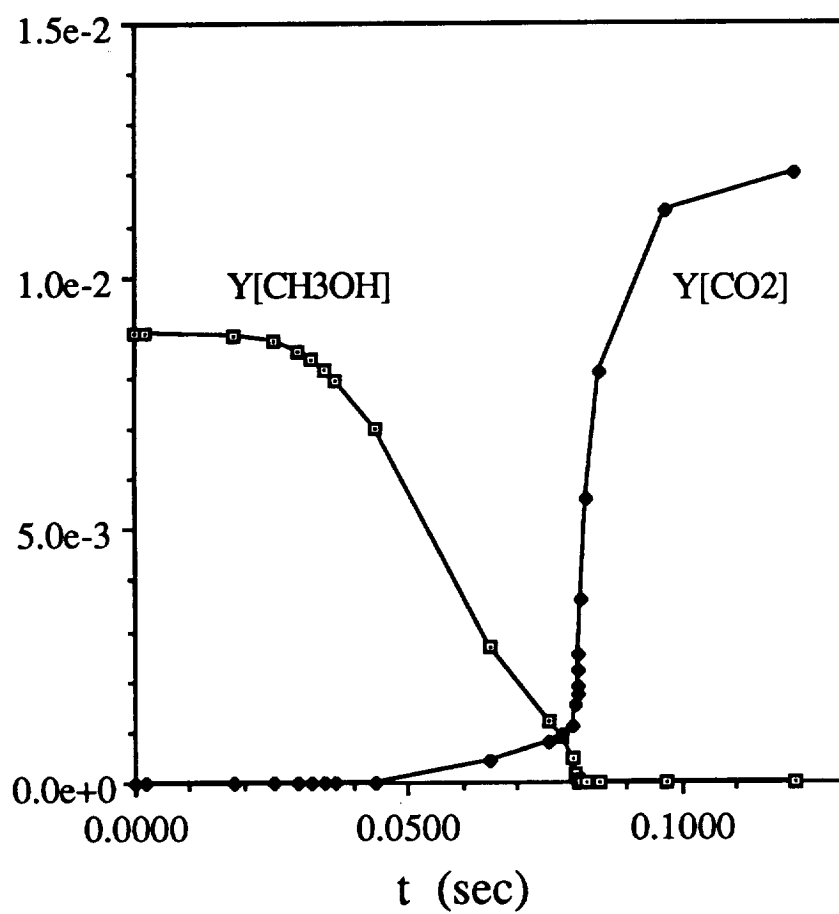
Fig. 1a. Mass Fractions of  $\text{CH}_3\text{OH}$  and  $\text{CO}_2$  vs. time.

Fig. 1b. Mass Fractions of CO and H vs. time – showing comparison of results of full and minimum sets discussed in §7.

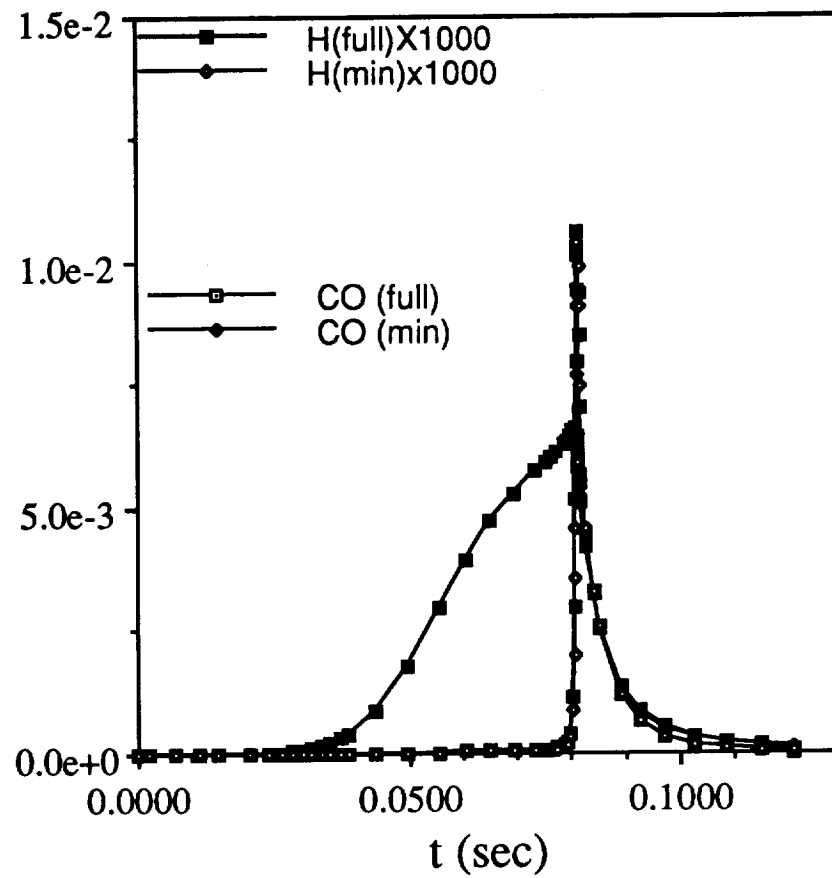


Fig. 2. Number of Exhausted Modes,  $M$ , vs. time.

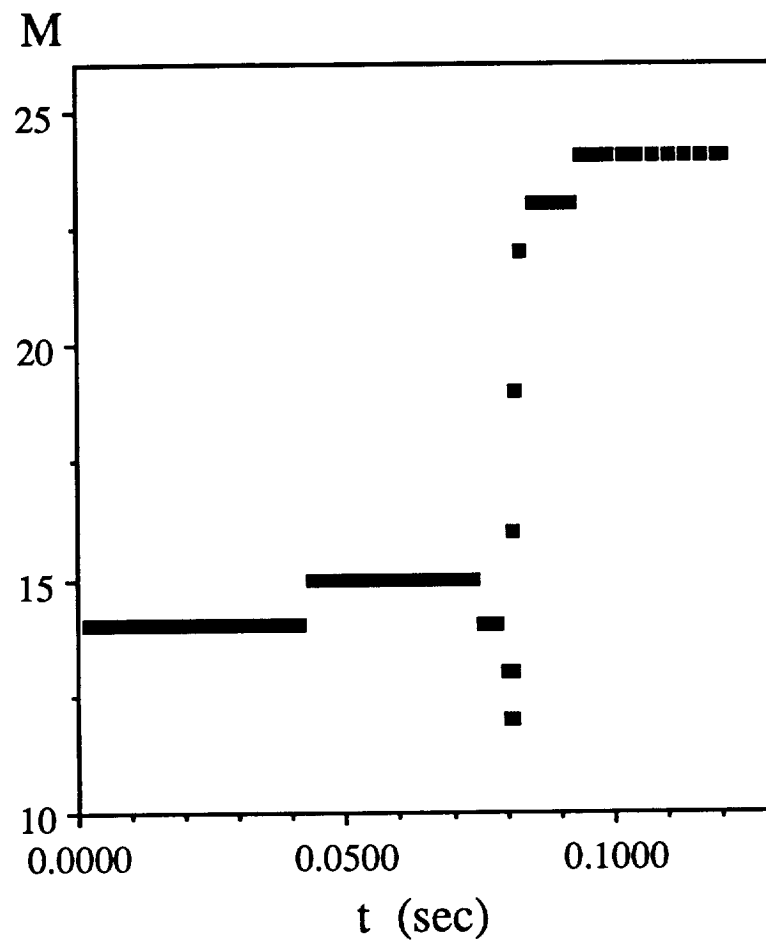


Fig. 3a. Importance Index for  $\text{CH}_3\text{OH}$ ,  $I_k^{15}$ , vs. time – for reactions involving  $\text{CH}_3\text{OH}$ .

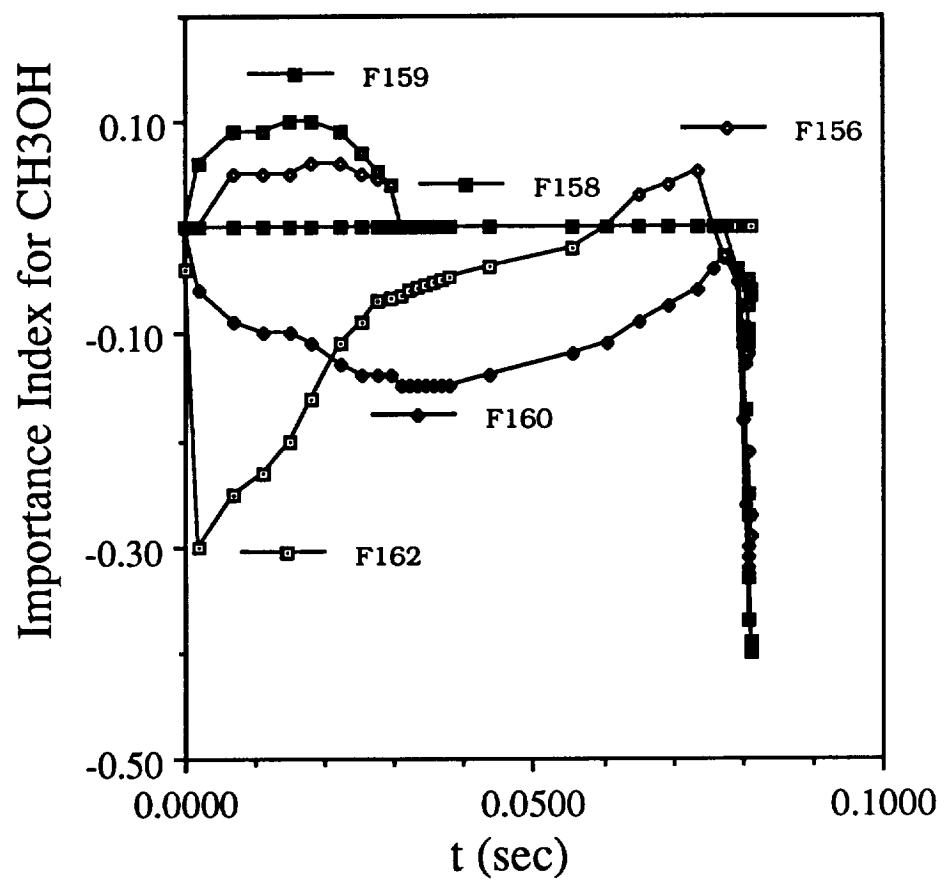
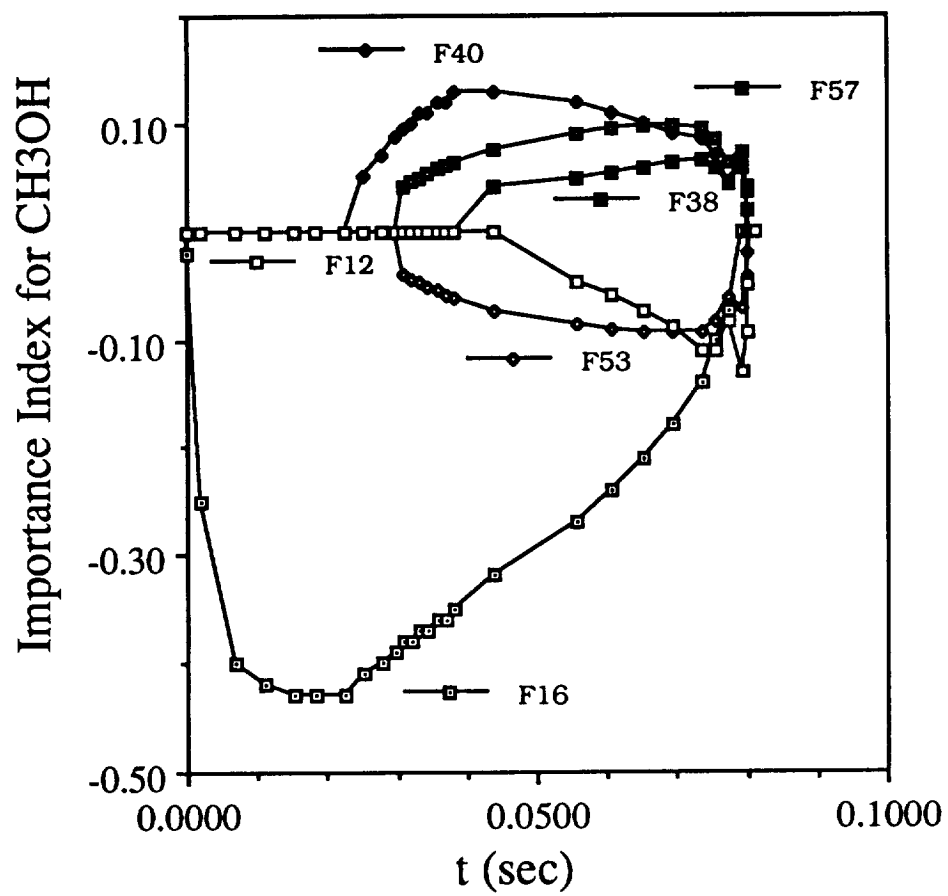


Fig. 3b. Importance Index for  $\text{CH}_3\text{OH}$ ,  $I_k^{15}$ , vs. time – for reactions *not* involving  $\text{CH}_3\text{OH}$ .



### References

- <sup>1</sup> Egolfopoulos, F. N., Du, D. X. and Law, C. K., to appear in Comb. Science and Tech. 1992.
- <sup>2</sup> Kee, R.J., Rupley, F.M. and Miller, J.A., Sandia Report SAND89-8009, 1989.
- <sup>3</sup> Lam, S. H., in *Recent Advances in the Aerospace Sciences*, Corrado Casci, Ed., Plenum Press, pp. 3-20, 1985.
- <sup>4</sup> Lam, S. H. and Goussis, D. A., *Proceedings of the 22nd International Symposium on Combustion*, pp. 931-941, U. of Washington, Seattle, Washington, August, 1988.
- <sup>5</sup> Lam, S. H. and Goussis, D. A., in *Reduced Kinetic Mechanisms and Asymptotic Approximations for Methane-Air Flames*, M. Smooke, Ed., Lecture Notes in Physics, Springer-Verlag, 1991.
- <sup>6</sup> Williams, F. A., "Combustion Theory," 2nd Edition, Benjamin/Cummings Publ. Co. 1985.
- <sup>7</sup> Peters, N., Symposium on Numerical Simulation of Combustion Phenomena, Sophia Antipolis, 1985.
- <sup>8</sup> Peters, N. and Williams, F. A., Combust. Flame, **68**, pp. 185-207, 1987.
- <sup>9</sup> Trevino, C., in Progress in Astronautics and Aeronautics, **131**, pp. 14-43, 1991.
- <sup>10</sup> Yetter, R. A., Dryer, F. L. and Rabitz, H., Comb. Sci. Tech., **79**, pp. 129-140, 1991.
- <sup>11</sup> Yetter, R. A. and Dryer, F. L., Combust. Flame, **59**, pp. 107-133, 1985.
- <sup>12</sup> Miller, D. and Frenklach, M., Intl J. Chem. Kinetics, **15**, pp. 677-696, 1983.
- <sup>13</sup> Goussis, D. A. and Lam, S. H., Princeton University MAE Report #1926, 1991.
- <sup>14</sup> Lam, S. H., and Goussis, D. A., presented at 4th Intl. Conference on Numerical Combustion, SIAM, St. Petersburg, Florida, 1991.

### **Appendix III**

#### **On Reacting FLOws with Diffusion and Fast Chemical Reactions**

Manuscript in Preparation



# On Reacting Flows with Diffusion and Fast Chemical Reactions\*

S. H. Lam

Department of Mechanical and Aerospace Engineering  
Princeton University, Princeton, N.J. 08544

Draft

## Abstract

When very fast chemical reactions are present in the study of reacting flows, the so-called partial-equilibrium and the quasi-steady approximations are frequently applied to simplify the chemical kinetics source terms, to remove stiffness, and to reduce the number of dependent variables. An important consequence of these approximations is that the mass diffusion term of the individual species must be simultaneously modified. This paper presents a general and systematic derivation of the modifications, including that of the boundary conditions, for massively complex chemically reacting flows using computational singular perturbation (CSP). Simple examples shall be used to demonstrate the theoretical concepts.

## 1 Introduction

In reacting flow problems, when vastly disparate chemical reaction time scales are present, the partial-equilibrium and/or quasi-steady approximations are frequently employed<sup>[1],[2],[3],[4],[5]</sup> to simplify the chemical reaction source

---

\*This work is supported by NASA Langley's Aerothermodynamics Branch, Space Systems Division.

term. Theoretically, the mass diffusion terms in the PDE's are concurrently affected by this simplification<sup>[6]</sup>. In the present paper, we shall present a unified derivation of the simplified equations, paying particular attention to the modified mass diffusion terms, including the modified boundary and initial conditions, under the assumption that the characteristic diffusion Péclet number of the problem is moderately large—*i.e.* the flow is primarily convection dominated, with diffusion being important mainly in relatively thin boundary layers.

The present work is an extension of the theory of *computational singular perturbation* (CSP)<sup>[7],[8],[9],[10]</sup>. While the existing CSP theory has been limited to a system of ODE's, the present extension includes spatial diffusion and deals for the first time with a system of PDE's. Anticipating that research in modern reacting gasdynamics will be strongly CFD oriented, some special numerical issues will also be addressed. It will be shown that the CSP methodology of *refinement* of basis vectors is directly applicable to this class of PDE problems, allowing the algorithmic treatment of massively complex convection-reaction-diffusion problems which contain exhausted fast reactions.

We shall first work through a simple example using conventional methodology, then present a formal extension of the CSP theory. Finally, the CSP methodology is applied to the example as a demonstration.

## 2 The General Statement of the Problem

We consider a reacting gasdynamics problem with  $N$  chemistry related unknowns. Let  $\mathbf{y}$  be the  $N$ -dimensional column vector representing the unknowns. The dot product operator of this  $N$ -dimensional space shall be denoted by " $\odot$ " to distinguish it from the ordinary "." of the 3-dimensional spatial dot operator. The general dimensional PDE system for  $\mathbf{y}$  can be expressed as follows:

$$\frac{D\mathbf{y}}{Dt} = \mathbf{g} + \mathbf{d}, \quad (1)$$

where  $\mathbf{g}(\mathbf{y})$  is the chemical reactions source term,  $\mathbf{d}$  is the mass diffusion term:

$$\mathbf{d} \equiv \nabla \cdot (\mathbf{D} \odot \nabla \mathbf{y}), \quad (2)$$

and  $\mathbf{D}$  is a  $N \times N$  matrix of diffusion coefficients (usually diagonal). Appropriate initial and boundary conditions for all  $N$  unknowns are provided.

The chemical reaction source term  $\mathbf{g}$  is usually expressed as the sum of  $R$  terms each representing an elementary reaction:

$$\mathbf{g} = \sum_{r=1}^R \mathbf{s}_r F^r, \quad (3)$$

where  $\mathbf{s}_r$  and  $F^r$  are the *stoichiometric vector* and the *reaction rate* for the  $r$ -th elementary reaction, respectively. In general,  $N \neq R$ , and in most practical situations  $R$  is significantly larger than  $N$ . However, it should be obvious that only  $N$  stoichiometric vectors are linearly independent. Hence, the right hand side of (3) can always be expressed in terms of  $N$  linearly independent  $\mathbf{s}_r$ 's serving as the "basis vectors" of the  $N$ -dimensional space.

In the modern age of CFD, solutions to such non-linear PDE problems can be obtained numerically. The main numerical issues are: the much larger number of unknowns in comparison to non-reacting gasdynamics, and the "stiffness" of the equations introduced by the disparate chemical time scales. So long as an adequate computing budget is available, these issues can be resolved. However, the amount of physical insights which can be extracted from numerical solutions is usually limited. In the present paper, we shall focus on the derivation of an approximate simplified non-stiff system of PDE's, including its boundary conditions. The rationale is that the knowledge of the approximate simplified equations, in addition to the solution itself, can provide much more physical insights than otherwise available.

## 2.1 Preliminary Discussion

When the problem under investigation is sufficiently simple, the conventional approach is to first non-dimensionalize the dependent and independent variables, obtain the dimensionless governing equations, and identify the relevant dimensionless Péclet numbers and Damköhler numbers. The initial task of non-dimensionalization requires considerable skill; order of magnitude estimates must be made intelligently, and intuition and experience of the investigator play a major role. In contrast, the subsequent task is relatively straightforward: develop an asymptotic theory in the limit of certain Damköhler numbers being infinitely large—assuming that all other dimen-

sionless parameters remain finite. In most applications, only “leading order” results are needed.

In using CFD to compute for the desired solutions, the flow domain of interest must first be covered by a suitable mesh or grid system. Let  $U$  be the local characteristic velocity of the flow field, and  $h$  the local characteristic cell width. The local characteristic *flow time*,  $\tau_{flow}$ , is:

$$\tau_{flow} \equiv \frac{h}{U}. \quad (4)$$

The local characteristic *diffusion time*,  $\tau_{diff}$ , is:

$$\tau_{diff} \equiv \frac{h^2}{D} \quad (5)$$

where  $D$  is a representative local diffusion coefficient. The ratio of  $\tau_{diff}$  to  $\tau_{flow}$  is the local Péclet number:

$$P_e(h) \equiv \frac{Uh}{D} \quad (6)$$

which is  $h$ -dependent. In the present paper, we shall assume the  $P_e(h_{max})$  is moderately large so that globally diffusion does not dominate convection.

When a chemistry source term  $\mathbf{g}$  is present, a number of chemical reaction time scales are introduced into the problem. It is obviously that their presence should have a significant impact on the grid system used for the computations. At the present time, no general theory exists to guide the selection of the appropriate local values of  $h$ . Usually, the grid is chosen by the investigator based by some informed expectations of the behaviors of the desired solutions. As a general principle, one would like to use as few grid points as possible without sacrificing accuracy and spatial resolution. Usually, a global upper limit  $h_{max}$  is placed on  $h$  so that the resulting numerical solution is assured of adequate spatial resolution.

The issue at hand is how to deal with reacting flow problems in which the characteristic time scales of some fast reactions are very, very small.

### 3 A Simple Example

Consider a simple reaction system consisting of two elementary reactions and two reactants  $A$  and  $B$ :

Reaction #1:



Reaction: #2:



The mass diffusion coefficients of  $A$  and  $B$  are denoted by  $D_A$  and  $D_B$ , respectively. The dimensional governing PDE for the two reactants are:

$$\frac{DA}{Dt} = -2F^1 - F^2 + \nabla \cdot (D_A \nabla A), \quad (8a)$$

$$\frac{DB}{Dt} = F^1 + F^2 + \nabla \cdot (D_B \nabla B), \quad (8b)$$

where  $D/Dt$  is the substantial derivative operator:

$$\frac{D}{Dt} \equiv \frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla, \quad (8c)$$

$\mathbf{v}$  is the flow velocity, and

$$F^1 \equiv k_1(A^2 - K_1 B), \quad (8d)$$

$$F^2 \equiv k_2(A - K_2 B). \quad (8e)$$

For the sake of simplicity, we shall assume that the rate coefficients  $k_1, k_2$ , equilibrium constants  $K_1, K_2$  are constants, the flow is steady, and that the characteristic Péclet number of the problem is moderately large so that (8a) and (8b) are essentially parabolic. At the upstream boundary, initial condition is provided. At the "side" and downstream boundary surfaces, appropriate boundary conditions are provided.

We are interested in deriving the simplified PDE's and their modified boundary conditions for this simple problem when one of the chemical reactions is very fast.

For the sake of concreteness, we shall assume that reaction #1 is the fast reaction.

The chemical reaction system also introduces time scales. When confronted by a large and complex chemical reaction system, however, the above theoretical task is simply not viable. Instead, theoreticians usually proceed by

intelligently applying *ad hoc* approximations which must be guided by intuition and experience. The so-called *partial equilibrium approximation* (PEA) requires that the theoreticians can somehow identify the fast reactions, the so-called *quasi-steady approximation* (QSSA) requires that the theoreticians can somehow identify the fast reactants (frequently called “radicals”). These conventional techniques will be demonstrated in the next sections, with special emphasis on the diffusion terms.

If  $M$  (linearly independent) reactions are assumed exhausted, the net reaction rates of these  $M$  reactions are set to zero. In addition,  $M$  species are judiciously identified as “radicals” and they are solve for in terms of the remaining  $N - M$  unknowns from the  $M$  algebraic equations obtained by PEA. The subsequent derivation of the leading order simplified equations requires some care, but is relatively straightforward. If  $M$  species can somehow be identified as radicals, the so-called *quasi-steady state approximation* (QSSA) is available. To apply QSSA, the convection term of the radicals are simply neglected.

If diffusive effects are absent, the simplification of this system of ODE's can be handled by existing methods. The focus of this paper is to show how diffusive effects should be handled.

For this simple problem, the dependent and the independent variables can be intelligently non-dimensionalized, and the appropriate asymptotic theory can be formally developed. the dimensional parameters are:  $L$ , the characteristic length scale,  $U$ , the characteristic velocity of the flow field, and  $D_A$ ,  $D_B$ ,  $k_1$ ,  $k_2$  and  $K_1$ , while  $K_2$  is dimensionless. The characteristic convection time scale  $\tau_{flow}$  is:

$$\tau_{flow} \equiv L/U. \quad (9)$$

We shall assume that all the diffusion coefficients have comparable magnitudes so that they can be represented by a single characteristic value  $D$ . The characteristic diffusion time  $\tau_{diff}$  is then:

$$\tau_{diff} \equiv L^2/D. \quad (10)$$

In addition, we denote the characteristic time scales of reactions #1 and #2 by  $\tau_1$  and  $\tau_2$ , respectively. We shall be interested in the case when

$$\tau_1 \ll \tau_2 \approx \tau_{flow} \leq \tau_{diff}. \quad (11)$$

The Damköhler number is  $\tau_{diff}/\tau_{chem}$ . Then the Péclet number  $P_\epsilon$  for the problem, defined as the ratio of  $\tau_{diff}$  to  $\tau_{flow}$ , is:

$$P_\epsilon \equiv \frac{UL}{D}. \quad (12)$$

By assuming that  $P_\epsilon$  is  $O(1)$  or larger, we exclude the case where diffusion may be the fastest process in main domain of the problem. The issue at hand is to derive a simplified governing PDE for this example problem when reaction #1, which is *somehow* known to be much faster than reaction #2, is already “exhausted.” The modifications to the diffusion terms *and* the modified boundary conditions are of particular interest.

### 3.1 The Partial-Equilibrium Approximation

The conventional derivation of the simplified PDE’s for the example problem using PEA would proceed as follows.

Reaction #1 is somehow identified as the fast reaction, and is assumed to be exhausted after a brief transient period (away from boundary surfaces). The exhaustion of reaction #1 implies that the net reaction rate  $F^1$  is small (but *not* zero) compared to either the forward or reverse rates which must therefore balance each other approximately. By setting

$$F^1 = k_1(A^2 - K_1B) \approx 0, \quad (13a)$$

which is an *equation of state*, an algebraic relation between  $A$  and  $B$ . We can solve  $B$  in terms of  $A$ , or *vice versa*:

$$B \approx \frac{A^2}{K_1}, \quad (13b)$$

or

$$A \approx \sqrt{K_1B}. \quad (13c)$$

It is important to emphasize that, in the PEA procedure, (13a) (and therefore (13b) and (13c)) must *never* be substituted into (8a) or (8b)—because (13a) is in fact obtained from (8a) or (8b) by taking the formal limit of  $k_1 \rightarrow \infty$ . See (17) later.

Adding (8a) and two times (8b), we obtain, *without* approximation:

$$\frac{D}{Dt}(A + 2B) = F^2 + \nabla \cdot (D_A \nabla A) + 2\nabla \cdot (D_B \nabla B), \quad (14)$$

which does not contain  $F^1$ . Goddard<sup>[6]</sup> called  $A + 2B$  the *reaction invariant* of reaction #1.

We can now eliminate either  $B$  or  $A$  by using either (13b) or (13c), respectively. Using (13b) in (14) to eliminate  $B$ , we obtain:

$$\frac{DA}{Dt} \approx \frac{K_1}{K_1 + 4A} F^2 + \frac{K_1}{K_1 + 4A} \nabla \cdot (D_{AB} \nabla A), \quad (15a)$$

where  $D_{AB}$  is given by:

$$D_{AB} \equiv D_A + 4A \frac{D_B}{K_1}, \quad (15b)$$

and  $F^2$  is approximately

$$F^2 \approx \frac{k_2 K_2}{K_1} A \left( \frac{K_1}{K_2} - A \right). \quad (15c)$$

Alternatively, using (13c) in (14) to eliminate  $A$ , we obtain:

$$\frac{DB}{Dt} \approx \frac{2\sqrt{B}}{\sqrt{K_1} + 4\sqrt{B}} F^2 + \frac{4\sqrt{B}}{\sqrt{K_1} + 4\sqrt{B}} \nabla \cdot (D_{BA} \nabla B), \quad (16a)$$

where  $D_{BA}$  is given by:

$$D_{BA} \equiv D_B + \sqrt{\frac{K_1}{B}} \frac{D_A}{4}, \quad (16b)$$

and  $F^2$  is approximately

$$F^2 \approx k_2 K_2 \sqrt{B} \left( \frac{\sqrt{K_1}}{K_2} - \sqrt{B} \right). \quad (16c)$$

Equations (15a) and (13b), or (16a) and (13c) which are their equivalents, are the simplified PDE's, obtained with the PEA method, valid in the flow field where the "infinitely fast" reaction #1 is exhausted. They are not valid in thin layers immediately adjacent to boundary surfaces where reaction #1 may be active. Hence, the initial and boundary conditions for (15a) or (16a) must be modified. In particular, they are required to satisfy the equation of state, (13a).

By comparing (8a) and (15a), we find:

$$F^1 \approx -\frac{K_1 + 2A}{K_1 + 4A} F^2 - \frac{2A}{K_1 + 4A} \nabla \cdot (D_A \nabla A) - \frac{K_1}{K_1 + 4A} \nabla \cdot (D_B \nabla B) \quad (17)$$



which is also consistent with (8b) and (16a). Note that (17) does *not* contradict (13a). Mathematically, it is a more accurate version of (13a)—the terms on its right hand side are the next “higher order” terms which were neglected in (13a) in comparison to the terms which contribute to  $F^1$  on the left hand side. Equation (17) shows clearly that when reaction #1 is exhausted, its net reaction rate  $F^1$  is not “zero;” in fact, its leading order value can be accurately expressed in terms of the currently active chemistry and diffusion terms.

### 3.2 The Quasi-Steady State Approximation

The conventional derivation of the simplified PDE’s for the example problem using QSSA would proceed as follows. Either  $A$  or  $B$  must first be identified as a “radical” somehow, and then the convective term in the corresponding PDE is neglected in comparison to the chemical source and the diffusion terms.

#### 3.2.1 The QSSA applied to $B$

Neglecting the convective term in (8b), we solve for  $F^1$  to yield:

$$F^1 \approx -F^2 - \nabla \cdot (D_B \nabla B). \quad (18)$$

Unlike (13a), Equation (18) is not an algebraic equation relating  $A$  and  $B$ ; instead, it is a PDE for  $B$ . Using (18) to eliminate  $F^1$  from (8a), we obtain:

$$\frac{DA}{Dt} \approx F^2 + \nabla \cdot (D_A \nabla A) + 2\nabla \cdot (D_B \nabla B). \quad (19)$$

In order to make further progress, we must take advantage of the fact that reaction #1 is known to be fast: the forward and reverse reaction rates contributing to  $F^1$  on the left hand side of (18) are much larger than the terms on its right hand side. Thus, (18) is consistent with (13a), and therefore (13b), to “leading order.” Using (13b) to eliminate  $B$  from (19), we obtain:

$$\frac{DA}{Dt} \approx F^2 + \nabla \cdot (D_{AB} \nabla A) \quad (20)$$

where  $F^2$  is given by (15c). Comparing (18) and (20) with (17) and (15a), it is seen that QSSA when applied to  $B$  agrees with PEA only when the

additional assumption

$$K_1 \gg 4A \quad (21)$$

is satisfied.

### 3.2.2 The QSSA applied to A

Neglecting the convective term in (8a), we can solve for  $F^1$  to yield:

$$F^1 \approx -\frac{1}{2}F^2 + \frac{1}{2}\nabla \cdot (D_A \nabla A). \quad (22)$$

Using similar procedures as above, we obtain:

$$\frac{DB}{Dt} \approx \frac{1}{2}F^2 + \nabla \cdot (D_{BA} \nabla B) \quad (23)$$

where  $F^2$  is given by (16c). Comparing (22) and (23) with (17) and (16a), it is seen that QSSA when applied to  $A$  agrees with PEA only when the additional assumption

$$K_1 \ll 4A \quad (24)$$

is satisfied.

### 3.2.3 Comments on The Conventional Derivations

The above analyses can formally be justified when  $k_1 K_1 \gg k_2 K_2$ ,  $A = O(K_1/K_2)$  and  $B = O(K_1/K_2^2)$ , and that the characteristic Péclet numbers are  $O(1)$  or larger. When the order of magnitude estimates are satisfied, the PEA is valid when  $K_2 = O(1)$ , the QSSA applied to  $A$  is valid when  $K_2 \ll 1$ , and the QSSA applied to  $B$  is valid when  $K_2 \ll 1$ . If the order of magnitude estimates are not satisfied, then the validity of the results becomes uncertain even when the inequality  $k_1 K_1 \gg k_2 K_2$  is guaranteed.

For massively complex realistic problems, it is not possible perform the formal asymptotic analysis. In its stead, the rationales justifying the approximations used must come from the accumulated intuition and experience of the investigators. While the validity of the approximations used can in principle be assessed by estimating or calculating the next higher order corrections, this is seldom done in practice.

### 3.3 The Modified upstream Condition

If the boundary condition specified at the upstream boundary is not consistent with the exhaustion of reaction #1, a thin “initial” layer will exist to allow the fast chemistry effects to run its course while the diffusive effects are expected to be negligible. The standard CSP “radical correction” procedure<sup>[9]</sup> can be used to obtain the modified initial condition near the upstream boundary.

### 3.4 The Modified Side Boundary Conditions

The simplified PDE’s derived above are valid (after the brief initial layer) over the whole physical space of interest except for thin layers adjacent to boundary surfaces. The actual boundary conditions specified on the boundary surfaces must be modified to yield the proper boundary conditions to be applied at the edge of the thin layers.

Let  $\eta$  denote the physical coordinate normal to the boundary surface, and  $\xi$  denote the physical coordinates which lie on the boundary surface. Within a thin layer adjacent to a boundary surface, the PEA and QSSA are not expected to be valid. Intuitively, the substantial time derivative term and the contribution of reaction #2 to the chemistry source term are expected to be small here—in comparison to that of reaction #1—and are therefore negligible. In other words, reaction #1 and diffusion balance each other here. Let the “leading order approximation” to  $A$  and  $B$  in this thin layer be denoted by  $A_{bl}$  and  $B_{bl}$ . We have:

$$0 \approx -2F^1 + \frac{\partial}{\partial \eta} \left( D_A \frac{\partial A_{bl}}{\partial \eta} \right), \quad (25a)$$

$$0 \approx +F^1 + \frac{\partial}{\partial \eta} \left( D_B \frac{\partial B_{bl}}{\partial \eta} \right), \quad (25b)$$

which are now ODE’s. The boundary conditions are:

$$A_{bl}(\xi, \eta = 0, t) = A_o(\xi, t), \quad (given), \quad (26a)$$

$$B_{bl}(\xi, \eta = 0, t) = B_o(\xi, t), \quad (given), \quad (26b)$$

$$A_{bl}^2(\xi, \infty, t) \approx K_1 B_{bl}(\xi, \infty, t), \quad (26c)$$

where (26c) is applied at the edge of the thin layer symbolically located at  $\eta \rightarrow \infty$ .

The "boundary" value of  $A$  near the boundary surface ( $\eta = 0^+$ ) is identified with the value of  $A_{bl}$  at the edge of the thin layer ( $\eta = \infty$ ). In other words, the boundary condition for (15a) is given by:

$$A(\xi, \eta = 0^+, t) \approx A_{bl}(\xi, \infty, t). \quad (27)$$

In the general case when  $D_A$  and  $D_B$  depend on  $A_{bl}$  and  $B_{bl}$ , numerical solution of (25a) and (25b) is needed to obtain the values at the edge of the thin layer.

For the special case when  $D_A$  and  $D_B$  are constants, explicit analytical results can be obtained. Adding (25a) and two times (25b), we have:

$$0 \approx \frac{\partial^2}{\partial \eta^2} (D_A A_{bl} + 2D_B B_{bl}), \quad (28)$$

and its analytic solution which remains bounded as  $\eta \rightarrow \infty$  is:

$$D_A A_{bl} + 2D_B B_{bl} = D_A A_o + 2D_B B_o. \quad (29)$$

Evaluating (29) at the edge of the thin layer and using (26c), we obtain  $A_{bl}(\xi, \infty, t)$ :

$$A_{bl}(\xi, \infty, t) \approx \frac{K_1}{4D_B} [\sqrt{D_A^2 + 8D_B(D_A A_o + 2D_B B_o)/K_1 - D_A}]. \quad (30)$$

which depends on  $A_o$ ,  $B_o$ ,  $D_A$  and  $D_B$ . The corresponding value of  $B_{bl}(\xi, \infty, t)$  is given by (26c).

## 4 Extending CSP to Include Diffusion

For a reacting flow problem with a massively complex chemistry source term, progress can only be made if the investigator has sufficient experience and insights to identify the appropriate PEA and QSSA approximations. Even after such identification is made, The above derivation is viable only for relatively simple systems because of the amount of algebra involved.

We shall extend the existing CSP methodology, which so far can only deal only with a system of ODE's, to convection-reaction-diffusion problems which are governed by a system of PDE's. The goal is to provide a unified algorithm to derive the simplified PDE's for massively complex problems.

### 4.1 The Basic Idea of CSP

The basic idea of CSP is to divide the  $N$ -dimensional  $\mathbf{g}$ -space into a fast and a slow subspace.

### 4.2 The Fast and Slow Subspace

Following the existing CSP theory, the column vector  $\mathbf{g}$ , the chemical source term, is formally divided into a fast and a slow components:

$$\mathbf{g} \equiv \mathbf{g}^{fast} + \mathbf{g}^{slow}. \quad (31)$$

The fast component  $\mathbf{g}^{fast}$  resides in a  $M$ -dimensional fast subspace which is spanned by a set of *trial* (column and row) basis vectors  $\mathbf{a}_m$  and  $\mathbf{b}^m$  satisfying the orthonormal condition:

$$\mathbf{b}^m \odot \mathbf{a}_n = \delta_n^m, \quad m, n = 1, 2, \dots, M. \quad (32)$$

The question of *how* the trial fast basis vectors are to be chosen will be addressed in the next sections. The value of  $M$  is determined by the user-specified desired spatial resolution of the solution. For example, if the detailed structure of the solution of length scale below  $\Delta$  is not of interest, then  $M$  is determined by the requirement that the local velocity times the slowest of the fast time scales in  $\mathbf{g}^{fast}$  be less than  $\Delta$ . In reacting CFD codes,  $\Delta$  would be the local grid size.

Using the *fast subspace projection matrix*,  $\mathbf{Q}(M)$ , defined by:

$$\mathbf{Q}(M) \equiv \sum_{m=1}^M \mathbf{a}_m \mathbf{b}^m, \quad (33)$$

we can express  $\mathbf{g}^{fast}$  in terms of  $M$  linearly independent modes:

$$\mathbf{g}^{fast} \equiv \mathbf{Q}(M) \odot \mathbf{g} \quad (34)$$

$$= \sum_{m=1}^M \mathbf{a}_m f^m, \quad (35)$$

where  $f^m$  is the *amplitude* of the  $m$ -th mode:

$$f^m \equiv \mathbf{b}^m \odot \mathbf{g}, \quad m = 1, 2, \dots, M. \quad (36)$$

The slow component  $\mathbf{g}^{slow}$  is simply the complementary component of  $\mathbf{g}$ :

$$\mathbf{g}^{slow} = (\mathbf{I} - \mathbf{Q}(M)) \odot \mathbf{g}. \quad (37)$$

The question to be answered is: what happens to  $f^m$  (and therefore to  $\mathbf{g}^{fast}$ ) when the fast reactions are “exhausted?”

### 4.3 The Asymptotic Solution for $f^m$

To answer the above question, we need to know what happens to  $f^m$  following a parcel of fluid. Taking the substantial derivative of  $f^m$ , we have:<sup>1</sup>

$$\frac{Df^m}{Dt} = \sum_{n=1}^M \Lambda_n^m (f^n - f_\infty^n) + \mathbf{b}^m \odot \mathbf{J} \odot \mathbf{d}, \quad m = 1, 2, \dots, M, \quad (38)$$

where

$$\mathbf{J} \equiv \frac{\partial \mathbf{g}}{\partial \mathbf{y}}, \quad (N \times N \text{ Jacobian matrix}), \quad (39a)$$

$$\Lambda_n^m \equiv \left( \frac{D\mathbf{b}^m}{Dt} + \mathbf{b}^m \odot \mathbf{J} \right) \odot \mathbf{a}_n, \quad m, n = 1, 2, \dots, M, \quad (39b)$$

$$f_\infty^m = -\mathbf{b}_o^m \odot (\mathbf{I} - \mathbf{Q}(M)) \odot \mathbf{g}, \quad m, n = 1, 2, \dots, M. \quad (39c)$$

Note that both the  $M \times M$  matrix  $\Lambda_n^m$  and the amplitudes  $f_\infty^m$  depend on the fast basis vectors chosen. It is clearly highly desirable for  $f_\infty^m$  to be as “small” as possible.

The theory of CSP generates from any reasonable set of trial basis vectors a new set of *refined* basis vectors with the desirable consequences. The refined (row) fast basis vectors,  $\mathbf{b}_o^m$ , are given by the CSP step #1 refinement procedure:<sup>[9],[10]</sup>

$$\mathbf{b}_o^m = \sum_{n=1}^M \tau_n^m \left( \frac{D\mathbf{b}^n}{Dt} + \mathbf{b}^n \odot \mathbf{J} \right), \quad m = 1, 2, \dots, M, \quad (40a)$$

and  $\tau_n^m$  is the inverse of  $\Lambda_n^m$ . The refined (column) fast basis vectors,  $\mathbf{a}_m^o$ , are given by the CSP step #2 refinement procedure:

$$\mathbf{a}_m^o = \sum_{n=1}^M \left( -\frac{D\mathbf{a}_n}{Dt} + \mathbf{J} \odot \mathbf{a}_n \right) \tau_{o,m}^n, \quad m = 1, 2, \dots, M, \quad (40b)$$

---

<sup>1</sup>The considerable amount of algebra involved in the derivation of (38), (39c) and (40a) is straightforward and is omitted here.

where  $\tau_{o,m}^n$  is the inverse of  $\Lambda_{o,m}^n$ . Note that these refined basis vectors automatically satisfy:

$$\mathbf{b}_o^m \odot \mathbf{a}_n = \delta_n^m, \quad m, n = 1, 2, \dots, M, \quad (41a)$$

and

$$\mathbf{b}_o^m \odot \mathbf{a}_n^o = \delta_n^m, \quad m, n = 1, 2, \dots, M. \quad (41b)$$

In essence, the refinement procedure described above is simply an extension of the so-called power method<sup>[11]</sup> for finding the largest (left and right) eigenvectors of a real matrix by iteration.

We shall use the CSP convention that superscript and subscript o indicate that the appropriate CSP-refined basis vectors are used<sup>[9]</sup>. For example, the new  $\mathbf{Q}_o^o(M)$  is given by:

$$\mathbf{Q}_o^o(M) \equiv \sum_{m=1}^M \mathbf{a}_m^o \mathbf{b}_o^m. \quad (42)$$

The eigen-values of the  $M \times M$  matrix  $\tau_n^m$  have the dimension of time, and can be interpreted as the time scales of the fast modes. In the theory of CSP, all  $M$  fast time scales are assumed asymptotically small in comparison to the currently active time scale. Let  $\tau(M)$  denote the slowest of the fast time scales, and let  $\tau(M+1)$  denote the fastest of the slow time scales which is of the same order as the fluid mechanics time scale. The parameter  $\epsilon(M)$  defined by:

$$\epsilon(M) \equiv \left| \frac{\tau(M)}{\tau(M+1)} \right| \quad (43)$$

is a measure of the *time scale separation* between the fast and slow subspace. The present theory, following the CSP theory for ODE's, formally assumes large time scale separation, *i.e.*  $\epsilon(M) \ll 1$ .

The right hand side of (1),  $\mathbf{g} + \mathbf{d}$ , can now be decomposed by using the refined basis vectors:

$$\frac{D\mathbf{y}}{Dt} = \mathbf{g} + \mathbf{h} = (\mathbf{g}_o^{o,fast} + \mathbf{d}_o^{o,fast}) + (\mathbf{g}_o^{o,slow} + \mathbf{d}_o^{o,slow}), \quad (44)$$

where

$$\mathbf{g}_o^{o,fast} + \mathbf{d}_o^{o,fast} = \mathbf{Q}_o^o(M) \odot (\mathbf{g} + \mathbf{d}), \quad (45a)$$

$$= \sum_{m=1}^M \mathbf{a}_m^o (f_o^m + \mathbf{b}_o^m \odot \mathbf{d}), \quad (45b)$$

$$f_o^m \equiv \mathbf{b}_o^m \odot \mathbf{g}, \quad m = 1, 2, \dots, M, \quad (45c)$$

$$\mathbf{g}_o^{o,slow} + \mathbf{d}_o^{o,slow} = (\mathbf{I} - \mathbf{Q}_o^o(M)) \odot (\mathbf{g} + \mathbf{d}), \quad (45d)$$

The issue at hand is to find the asymptotic solution for  $(\mathbf{g}_o^{o,fast} + \mathbf{d}_o^{o,fast})$ , and to show that it can be neglected in (44) after a brief initial transient.

Using (31), (35) and (37) in (45c), the fast mode amplitudes  $f_o^m$  can be expressed as:

$$f_o^m = f^m - f_\infty^m, \quad (46)$$

Using (46) to eliminate  $f^m$  from (38), we obtain:

$$\frac{Df_o^m}{Dt} = \sum_{n=1}^M \Lambda_n^m (f_o^n - (f_{o,\infty}^n - \mathbf{b}_o^n \odot \mathbf{d})), \quad (47)$$

where

$$f_{o,\infty}^n \equiv \sum_{m=1}^M \tau_m^n \left( \frac{Df_\infty^m}{Dt} + \frac{D\mathbf{b}_o^m}{Dt} \odot \mathbf{d} \right). \quad (48)$$

In contrast to  $f_\infty^m$ , which is *not* guaranteed to be small in the small  $\epsilon(M)$  limit,  $f_{o,\infty}^m$  is formally  $O(\epsilon(M))$  in the small  $\epsilon(M)$  limit provided that  $\mathbf{d}$  is of order unity.

Assuming that all eigen-values of  $\Lambda_n^m$  are essentially negative, we can conclude that the leading order asymptotic solution to (47) is:

$$f_o^m \approx f_{o,\infty}^m - \mathbf{b}_o^m \odot \mathbf{d}, \quad m = 1, 2, \dots, M, \quad (49)$$

which is valid after a brief initial transient (following the trajectory of a fluid parcel). Using (49) in (44) and (45b), we obtain:

$$\frac{D\mathbf{y}}{Dt} \approx \sum_{m=1}^M \mathbf{a}_m^o f_{o,\infty}^m + (\mathbf{I} - \mathbf{Q}_o^o(M)) \odot (\mathbf{g} + \mathbf{d}). \quad (50a)$$

and

$$\mathbf{g}_o^{o,fast} + \mathbf{d}_o^{o,fast} \approx \sum_{m=1}^M \mathbf{a}_m^o f_{o,\infty}^m. \quad (50b)$$

Both (50b) and (50a) are valid after the brief initial transient layer.



By neglecting  $f_{o,\infty}^m$  in the small  $\epsilon(M)$  limit from (50b) and (50a), we obtain:

$$\frac{Dy}{Dt} \approx (\mathbf{I} - \mathbf{Q}_o^o(M)) \odot (\mathbf{g} + \mathbf{d}). \quad (51a)$$

$$\mathbf{g}_o^{o,fast} + \mathbf{d}_o^{o,fast} \approx 0, \quad (51b)$$

The solution of (51a) automatically satisfies (51b) for  $t > t_o$  in the Lagrangian sense, provided that it is satisfied at  $t = t_o$ .

By neglecting  $f_{o,\infty}^m$  in the small  $\epsilon(M)$  limit from (49), we obtain:

$$f_o^m \approx -\mathbf{b}_o^n \odot \mathbf{d}, \quad m = 1, 2, \dots, M. \quad (52)$$

However, except inside a very thin reaction-diffusion layer adjacent to boundaries,  $(\mathbf{b}_o^n \odot \mathbf{d})$  in (52) is itself a “higher order” term in comparison to the individual terms which contribute to  $f_o^m$ . Hence external to this thin layer,  $(\mathbf{b}_o^n \odot \mathbf{d})$  can be neglected to obtain  $M$  algebraic relations between the components of  $\mathbf{y}$ :

$$f_o^m \approx 0, \quad m = 1, 2, \dots, M, \quad (53)$$

which are called *equations of state* in the theory of CSP. However, this higher order term  $(\mathbf{b}_o^n \odot \mathbf{d})$  must be kept in (52) in the derivation of (51b) and (51a) above.

A variant of (50a) was derived by Maas and Pope<sup>[12]</sup> who called their approach the method of *intrinsic low-dimensional manifold* (ILDM)<sup>[13]</sup>. Instead of the CSP-refined basis vectors, they used the local fast eigen-vectors of  $\mathbf{J}$  to evaluate the fast subspace projection matrix. In addition, they chose not to use (37) for the evaluation of  $\mathbf{g}_o^{o,slow}$ , and handled the right hand side of (50a) differently. A discussion of their approach can be found in published comments which followed the paper in reference [12].

The remaining question to be resolved is the modified boundary condition for (50a).

#### 4.4 The Reaction-Diffusion Layer

Immediately adjacent to physical boundaries, the user-specified boundary conditions may not be consistent with (53), and the fast modes are in general active there. A very thin layer therefore exists in which mass diffusion

balances fast chemistry. We shall denote the solution in this thin layer by  $\mathbf{y}_{bl}$ , the local coordinates on the boundary surface by  $\xi$  and  $\eta$  as defined previously.

In this reaction-diffusion layer, we rewrite (1) as follows:

$$\mathbf{d} = -\mathbf{g} + \frac{D\mathbf{y}_{bl}}{Dt}. \quad (54)$$

The diffusion term  $\mathbf{d}$  can be approximated by:

$$\mathbf{d} \approx \frac{\partial}{\partial \eta} (\mathbf{D} \odot \frac{\partial \mathbf{y}_{bl}}{\partial \eta}). \quad (55)$$

The right hand side of (54) can be decomposed into its fast and slow components using the refined basis vectors:

$$\frac{\partial}{\partial \eta} (\mathbf{D} \odot \frac{\partial \mathbf{y}_{bl}}{\partial \eta}) \approx (-\mathbf{g} + \frac{D\mathbf{y}_{bl}}{Dt})_o^{o,fast} + (-\mathbf{g} + \frac{D\mathbf{y}_{bl}}{Dt})_o^{o,slow}. \quad (56)$$

Neglecting the slow component and the convective term in the fast component, we obtain the leading order governing equation for the thin reaction-diffusion layer:

$$\frac{\partial}{\partial \eta} (\mathbf{D} \odot \frac{\partial \mathbf{y}_{bl}}{\partial \eta}) \approx -\mathbf{g}_o^{o,fast}. \quad (57)$$

Equation (57) is a system of  $N$  second order ODE's and it poses a two-point boundary-value problem. The “initial” value for  $\mathbf{y}_{bl}$  at  $\eta = 0$  is known from the original boundary condition. Since (57) is invariant under the transformation  $\eta \rightarrow -\eta$ , “decaying” and “explosive” modes will appear in pairs. The CSP initial-value algorithm can be adapted to handle this special class of “infinite horizon” boundary layer problems<sup>[14]</sup>—the explosive modes can be explicitly suppressed using CSP methodology.

The “thickness” of the layer,  $\Delta\eta$ , is of the order of  $O(\sqrt{D_{max}\tau(M)})$  where  $D_{max}$  is the largest eigen-value of  $\mathbf{D}$ . It can be considered a “thin” layer whenever  $\Delta\eta \ll L$  where  $L$  is the characteristic length scale of the given physical problem. The edge of the layer, denoted by  $\eta \rightarrow \infty$ , is located at the point when all  $M$  fast modes are declared exhausted. The solution of the thin layer equation, (57), remains constant beyond this point, and is identified as  $\mathbf{y}_{bl}(\xi, \infty, t)$ .

The boundary condition for (50a) is:

$$\mathbf{y}(\xi, \eta = 0^+, t) = \mathbf{y}_b(\xi, \infty, t). \quad (58)$$

It is perhaps interesting to note that the value of  $\mathbf{y}_b(\xi, \infty, t)$  cannot be obtained by the so-called *radical correction*<sup>[9],[10]</sup> using the refined basis vectors obtained for the PDE's—unless all mass diffusion coefficients are identical.

#### 4.5 The Initial Transient Layer

In the initial transient layer, the effect of mass diffusion is generally negligible and therefore can be treated by the radical correction as demonstrated in reference [10].

### 5 The Simple Example Revisited

To get started, we can use either the fast eigen-vectors of  $\mathbf{J}$  or the chemical stoichiometric vectors of the (guessed) fast reactions as our trial fast basis vectors. For our simple example, we consider reaction #1 to be the fast reaction:

$$\mathbf{a}_1 = [-2, 1]^T, \quad \mathbf{b}^1 = [-1, -1]. \quad (59)$$

The CSP step #1 refinement yields:

$$\mathbf{b}_o^1 = \frac{1}{K_1 + 4A} [-2A, K_1]. \quad (60)$$

The CSP step #2 refinement yields:

$$\mathbf{a}_1^o \approx [-2 + O(\epsilon(1)), 1 + O(\epsilon(1))]^T. \quad (61)$$

where the time scale separation parameter  $\epsilon(1)$  is proportional to  $k_2/k_1(K_1 + 4A)$ . It is seen that the refined  $\mathbf{a}_1^o$  can be approximated by the trial  $\mathbf{a}_1$  in the limit of  $k_1 \rightarrow \infty$  when  $\epsilon(1)$  is a small parameter. This will always be the case whenever the trial column basis vectors have been “judiciously” chosen. In fact, the closeness of  $\mathbf{a}_m$  and  $\mathbf{a}_m^o$  can be used in general as a “test” of how good the original choice of the trial vectors were. In practice, one should

proceed with the CSP analysis only when  $\mathbf{a}_m$  is a good approximation to  $\mathbf{a}_m^\circ$ . It can easily be verified that if the trial basis vectors were randomly chosen, the refined basis vectors will rapidly converge—if  $\epsilon(M)$  is small—after a few full cycles of CSP refinements.

For the sake of simplicity, we shall omit here the  $O(\epsilon(1))$  term in the fast subspace projection matrix:

$$\mathbf{Q}_o^\circ(1) \approx \frac{1}{K_1 + 4A} \begin{pmatrix} 4A & -2K_1 \\ -2A & K_1 \end{pmatrix}. \quad (62)$$

The corresponding slow subspace projection matrix is:

$$\mathbf{I} - \mathbf{Q}_o^\circ(1) \approx \frac{1}{K_1 + 4A} \begin{pmatrix} K_1 & 2K_1 \\ 2A & 4A \end{pmatrix}. \quad (63)$$

The analytical developments in §3 which assumed reaction #1 is fast can readily be reproduced by appropriately using these two projection matrices. For example: (15a) is the first component of (51a), (13b) is (53) with  $M = 1$ , (25a) and (25b) are “leading order” versions of (57) with  $N = 2$ .

## 6 Discussion

Mathematically, the above general theoretical development is an asymptotic analysis of a singularly perturbed problem in the limit of  $\epsilon(M) \rightarrow 0$  where  $\epsilon(M)$  is the ratio of the slowest exhausted fast time scale to the current time scale. Unlike the original CSP theory which is capable of including higher order terms by recursive applications, the present extension for PDE's is limited to only the leading order approximation. In return for this concession, the governing ODE's in the very thin reaction-diffusion layer are cleanly decoupled from the PDE's governing the rest of the flow field.

The value of  $f_{o,\infty}^n$  as given by (48) should be monitored in the course of the computation. Its value should be “small,” and may be included in (50a) and (50b) to improve the accuracy of the solution. If this small correction term is found to be significant, then one or more of the exhausted fast modes is reviving and the value of  $M$  should be decreased. In general, the updating of  $M$  along a fluid streamline can be dealt with in the standard manner. When an energy equation is included in the original model, then the term representing thermal conduction must also be appropriately modified<sup>[9]</sup>.

In a viscous boundary layer near a solid boundary, the flow field velocity is small as a consequence of the no-slip condition, and increases rapidly with  $\eta$ . In addition, the temperature profile in a thermal boundary layer is often also rapidly varying. As a consequence, the value of  $M$  and the identification of the fast reactions are expected to vary significantly across the viscous and thermal boundary layers. In the very thin reaction-diffusion layer, however, the flow velocity does not enter and the temperature is expected to be approximately the wall temperature. While theoretically the identification of the fast reactions can change across this layer, no strong variation is expected. In the present presentation, we have tacitly made the *ad hoc* assumption that the reduced reaction system representing  $\mathbf{g}_o^{o,fast}$  at the edge is valid throughout the very thin reaction-diffusion layer.

An important assumption in the present theoretical development is that all eigen-values of  $\Lambda_n^m$  are essentially negative. In other words, the fast modes are assumed to be decaying modes. If  $\Lambda_n^m$  does contain positive eigen-values, then the use of (49) will also suppress the fast "explosive modes." Such modes are physically essential and must be "unleashed" to describe certain important processes such as the ignition of flames. In addition, when  $\Lambda_n^m$  contains essentially imaginary eigen-values, then the use of (49) will also suppress the fast "oscillatory modes." The proper treatment of fast explosive or oscillatory modes which must not be suppressed is a difficult matter and is not yet adequately addressed by CSP at this time.

## References

- [1] Williams, F.A.; *Combustion Theory, The fundamental theory of chemically reacting systems*, 2nd edition, Benjamin/Cummings Publ. Co., Menlo Park, Ca., 1985.
- [2] Benson, S. W.; "The induction period in chain reactions," J. Chem. Phys., 20, p.1605, 1952.
- [3] Bowen, J. R., Acrivos, A. and Oppenheim, A. K.; "Singular perturbation refinement to quasi-steady state Approximation in chemical kinetics," Chem. Eng. Sci., 18, p.177, 1963.

- [4] Peters, N.; "Numerical simulation of combustion phenomena," Glowinski, R., Larrouurou, B and Temem, R., Eds., *Lecture Notes in Physics* 241, p. 90-109, Springer-Verlag, New York, 1985.
- [5] Peters, N. and Williams F. A.; "The asymptotic structure of stoichiometric methane-air Flames", *Combust. Flame*, **68**, pp. 185-207, 1987.
- [6] Goddard, J. D.; "Consequences of the Partial-Equilibrium Approximation for Chemical Reaction and Transport," *Proc. R. Soc. Lond.A*, pp. 271-284, 1990.
- [7] Lam, S. H.; "Singular perturbation for stiff equations using numerical methods", in *Recent Advances in the Aerospace Sciences*, Corrado Casci, Ed., Plenum Press, New York and London, pp.3-20, 1985.
- [8] Lam, S. H. and Goussis, D. A.; in *Reduced Kinetic Mechanisms and Asymptotic Approximations for Methane-Air Flames*, Chapter 10: "Conventional asymptotics and computational singular perturbation for simplified kinetics modeling," *Lecture Notes in Physics* 384, M. Smooke, Ed., Springer-Verlag, 1992.
- [9] Lam, S. H.; "Using CSP to understand complex chemical kinetics," to appear in *Combustion Science and Technology*, **89**, pp. 375-404, 1993. See Appendix I of this Final Report.
- [10] Lam, S. H. and Goussis, D. A.; "The CSP method for simplifying Kinetics," Manuscript in preparation. See Appendix IV of this Final Report.
- [11] Carnahan, B, Luther, H. A. and Wilkes, J. O.; *Applied Numerical Methods*, John Wiley and Sons, New York, 1969.
- [12] Maas, U. and Pope, S. B.; "Implementation of simplified chemical kinetics based on intrinsic low-dimensional manifolds," *Proceedings of the 24th International Symposium on Combustion*, University of Sydney, Sydney, Australia, July 5-10, 1992.
- [13] Maas, U. and Pope, S. B.; "Simplifying Chemical Kinetics: Intrinsic Low-Dimensional Manifolds in Composition Space," *Combust. Flame*, **88**, pp. 239-264, 1992.

- [14] Tron, A.; private communication, 1992.

## **Appendix IV**

### **The CSP Method for Simplifying Chemical Kinetics**

Manuscript in Preparation



# The CSP Method for Simplifying Kinetics\*

S. H. Lam† and D.A. Goussis‡

Department of Mechanical and Aerospace Engineering

†Princeton University, Princeton, N.J. 08544, U.S.A.

‡University of Patra, Patra, Greece

Draft

## Abstract

The *Computational Singular Perturbation* (CSP) method of simplified kinetics modeling is reviewed with emphasis on the justification of the methodology. A simple example is first worked through using the conventional methodology of partial-equilibrium and quasi-steady approximations, and then treated in some detail using CSP.

## 1 Introduction

When one is confronted with an unfamiliar problem in chemical kinetics, the traditional first step is to identify the relevant chemical species and the important elementary reactions which occur among them. The resulting “complete model” of the reaction system is usually further simplified to take advantage of available approximations. For sufficiently simple problems, conventional analytical methods can be used<sup>[1],[2],[3],[4],[5]</sup>. In most situations, the success of the resulting simplified model is measured not only by its quantitative predictive capability, but also by its simplicity—the fewer superfluous terms the better. Generally speaking, approximate analytical results are highly valued because of the insights they can provide when inspected by a competent

---

\*This work is supported by NASA Langley's Aerothermodynamics Branch, Space Systems Division.

theoretician. But when the reaction system is massively complex, this is not a practical option.

Recently, databases containing extensive, reliable and up-to-date data for certain reaction systems are available. Computations using complete models from such databases can now be routinely carried out. In this new computational era, it is no longer necessary to pick out only the relevant chemical species and the important elementary reactions—because the presence of benign superfluous terms in the formulation is not a problem. An option increasingly available to the modern theoretician is to first generate a complete model numerical solution, examine the resulting data to discern significant and interesting causes and effects, making additional diagnostic runs if necessary, and then try to propose simplifications and approximations. Why do theoreticians still care about simplified approximate models when double-precision numerical solutions to the complete model are easily available? The reasons are: physical understanding and “stiffness.” A theoretician would like to be able to make general statements about the problem in addition to showing color slides of the numerical solutions. The observed behaviors of the computed solutions need to be described in terms of familiar concepts, such as chain-branching, chain-termination, ignition delay, building up of the radical pool, heat release etc. In particular, theoreticians would also like to be able to identify the rate-controlling reactions (for the chemical species of interest in the time interval of interest), fast reactions for which rate coefficients do not need to be known accurately, and superfluous reactants and reactions which need not be included at all. In addition, the vast disparity of time scales which is responsible for the simplifications and approximations is also responsible for stiffness<sup>[6]</sup>, a generally undesirable attribute of the governing differential equations from the computation point of view.

The theory of *computational singular perturbation*<sup>[7],[8],[9],[10],[11],[12]</sup> (to be referred to as CSP here) exploits the power of the computer to do simplified kinetics modeling. In essence, CSP is a systematic mathematical procedure to do boundary-layer type singular perturbation analysis. While it can be used to obtain analytical results for simple problems, it is designed to be used for massively complex problems using computations. A CSP computation not only generates the numerical solution of the given problem, but also the *simplified equations* in terms of the given information. Most interesting questions about the reaction systems can be answered merely by inspection

of the numerical CSP data.

The present paper is a review of the theory of CSP. The basic CSP results are summarized, and are applied to a simple example to illustrate the essential features.

## 2 The Mathematical Problem

We shall consider a spatially homogeneous reaction system consisting of  $R$  elementary chemical reactions. The total number of unknowns, which include concentrations of the chemical species and other state variables such as temperature and total pressure, is  $N$ . We shall represent the  $N$  unknowns by a  $N$ -dimensional column vector,  $\mathbf{y} = [y^1, y^2, \dots, y^N]^T$ . The governing equation for  $\mathbf{y}$  is a system of quasi-linear ODE:

$$\frac{d\mathbf{y}}{dt} = \mathbf{g}(\mathbf{y}), \quad (2.1)$$

where  $\mathbf{g}$  is the sum of contributions from the  $R$  elementary reactions:

$$\mathbf{g} \equiv \sum_{r=1}^R \mathbf{s}_r F^r(\mathbf{y}), \quad (2.2)$$

and  $\mathbf{s}_r$  and  $F^r(\mathbf{y})$  are the (generalized) *stoichiometric vector* and the *reaction rate* of the  $r$ -th elementary reaction, respectively. The value of  $R$  may be greater, less than, or equal to  $N$ . We shall call (2.2) the *physical representation* of  $\mathbf{g}$ , because each additive term can be satisfactorily explained by the investigator who formulated the problem.

Usually, an investigator is interested only in certain special species, each with a different accuracy requirement and perhaps in a different time interval. In many cases, not all the initial conditions needed to compute the solutions are known, and many rate constants needed in the computations are only educated estimates. The mathematical problem is to derive the simplest model of the reaction system consistent with the user-specified accuracy requirements.

### 3 Some Definitions

When the forward and reverse reaction rates of a single or a group of fast reactions are in approximate balance, we say the reaction or the reaction group is in *partial-equilibrium*. When the production and destruction rates of a particular species are in approximate balance, we say the species is in *quasi-steady* state. In either case, an approximate algebraic relation is obtained between components of the  $\mathbf{y}$  vector. Such relations, which do *not* contain free parameters, shall be called *equations of state*. In many cases, species in quasi-steady state are chemical radicals, but not always.

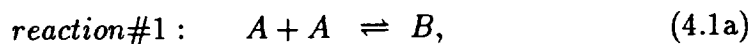
When  $M$  equations of state are available, they can be used to selectively solve for  $M$  unknowns in terms of the others—in so doing the need for  $M$  of the ODE's is eliminated. Which  $M$  unknowns should be solved for in terms of others, and which  $M$  ODE's should be discarded? Lam<sup>[12]</sup> provides explicit theoretical guidance to make these choices, and calls the  $M$  unknowns *CSP radicals*, or simply radicals for short, when they can be accurately solved for from the  $M$  equations of state. When used in this CSP context, the term radical carries a special meaning distinct from the context of chemical structure. In most situations, a CSP radical is also a chemical radical, and vice versa. But it is not always true. The identification of CSP radicals is done via a “radical pointer” which shall be demonstrated later.

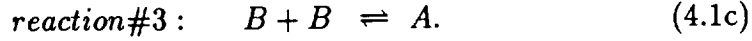
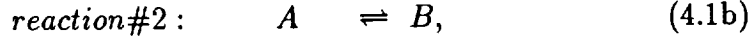
Frequently, additional (exact or approximate) algebraic relations between the components of the  $\mathbf{y}$  vector may exist. The conservation law of atomic species is one such example. Such relations are distinguished from the above equations of state by the presence of free parameters which are determined by initial conditions. Following Lam<sup>[12]</sup>, we shall call all such relations *conservation laws*.

### 4 A Simple Example

We shall use a simple hypothetical reaction system<sup>[12]</sup> to illustrate the issues involved.

Let the state vector be  $\mathbf{y} = [A, B, C]^T$  where  $A$  and  $B$  are chemical concentrations and  $C$  is temperature. The reaction system consists of three elementary reactions:





The (generalized) stoichiometric vectors and the reaction rates are:

$$\mathbf{s}_1 = [-2, 1, \Delta H_1]^T, \quad F^1 = k_1(A^2 - K_1 B), \quad (4.2a)$$

$$\mathbf{s}_2 = [-1, 1, \Delta H_2]^T, \quad F^2 = k_2(A - K_2 B), \quad (4.2b)$$

$$\mathbf{s}_3 = [1, -2, \Delta H_3]^T, \quad F^3 = k_3(B^2 - K_3 A). \quad (4.2c)$$

where the reaction rate coefficients  $k_1, k_2, k_3$  and the equilibrium constants  $K_1, K_2, K_3$  are known and—for the sake of simplicity—their dependence on  $C$  is assumed negligible. The heats of reaction (with the proper units) for the three reactions are denoted by  $\Delta H_1, \Delta H_2$  and  $\Delta H_3$ , respectively. We shall find it useful to separately identify the forward and reverse reaction rates as follows:

$$F^r = F_+^r - F_-^r, \quad r = 1, 2, \dots, R, \quad (4.3)$$

where  $F_+^r$  and  $F_-^r$  are both positive.

The system of ODE is:

$$\frac{dy}{dt} = \mathbf{s}_1 F^1 + \mathbf{s}_2 F^2 + \mathbf{s}_3 F^3, \quad (4.4)$$

which can be written out as follows:

$$\frac{dA}{dt} = -2F^1 - F^2 + F^3, \quad (4.5a)$$

$$\frac{dB}{dt} = F^1 + F^2 - 2F^3, \quad (4.5b)$$

$$\frac{dC}{dt} = \Delta H_1 F^1 + \Delta H_2 F^2 + \Delta H_3 F^3. \quad (4.5c)$$

To make things concrete, the rate coefficients are given numerical values:

$$k_1 \approx 10^4 \text{cc/mole-second}, \quad K_1 \approx 1.1 \times 10^{-2} \text{mole/cc}, \quad (4.6a)$$

$$k_2 \approx 10^{-1} \text{/second}, \quad K_2 \approx 1.1 \times 10^2, \quad (4.6b)$$

$$k_3 \approx 10^4 \text{cc/mole-second}, \quad K_3 \approx 0.8 \times 10^{-8} \text{mole/cc}, \quad (4.6c)$$

and

$$\Delta H_1 \approx +1.1 \times 10^4 \text{cc-}^\circ K/\text{mole}, \quad (4.7a)$$

$$\Delta H_2 \approx +1.0 \times 10^5 \text{cc-}^\circ K/\text{mole}, \quad (4.7b)$$

$$\Delta H_3 \approx -2.9 \times 10^5 \text{cc-}^\circ K/\text{mole}. \quad (4.7c)$$

The initial conditions are also given numerical values:

$$A(0) \approx 1.5 \times 10^{-4} \text{mole/cc}, \quad B(0) \approx 0.1 \times 10^{-6} \text{mole/cc}, \quad C(0) \approx 300^\circ K. \quad (4.8)$$

The investigator is interested in  $A(t)$ , accurate to two significant figures, after the first few seconds up to a few minutes.

Experience and intuition can play no role here because the problem is hypothetical, and indeed may not even make “chemical sense.” Note that detailed balance would require  $K_3 = K_1/(K_2)^3$ , thermodynamics would require  $\Delta H_3 = \Delta H_1 - 3\Delta H_2$ , and the Law of Mass Action would require  $s_r$  and  $F^r$  to be consistent. The data provided do not satisfy some of these relations exactly—they were chosen to demonstrate that the techniques under discussion are completely mathematical, and do not require consistency with constraints “external” to the given initial-value problem.

Because this example is sufficiently simple, a conventional asymptotic analysis can be performed—provided that the dependent and independent variables can be intelligently non-dimensionalized, and a small dimensionless parameter can be identified. The reader can readily confirm that even for this simple problem the task of non-dimensionalization of variables is not straightforward. Consequently, the conventional method usually proceeds with a dimensional formulation without the benefits of dimensionless parameters. Progress is made via intuitive *ad hoc* judgment on the speed rankings of the elementary reactions, and the use of partial-equilibrium or quasi-steady approximations must follow certain special procedures. We shall illustrate the conventional methodology in the following section.

## 5 The Conventional Methodology

We shall demonstrate the partial-equilibrium approximation first, followed by the quasi-steady approximation.

### 5.1 The Partial-Equilibrium Approximation

For the example problem, a competent investigator will (correctly) conclude that reaction #1 is fastest, reaction #2 is next, and reaction #3 is slowest. In the time period of interest, it is expected that reaction #1 will have

exhausted itself, reaction #2 is the rate-controlling reaction, and reaction #3 is essentially dormant.

**Reaction #1 is exhausted:** The partial-equilibrium approximation for reaction #1 consists of setting the net reaction rate of reaction #1 to zero. The following equation of state is obtained:

$$F^1 = k_1(A^2 - K_1B) \approx 0, \quad (5.1)$$

Note that (5.1) contains no free parameters. One may use it to solve  $A$  in terms of  $B$ , or  $B$  in terms of  $A$ .

Equation (5.1) must be handled with care—it must *never* be substituted directly into the original system of equations. If this advice is not heeded and (5.1) is substituted into (4.5a), (4.5b) and (4.5c), the resulting equations are simply wrong. This is because the small net reaction rate of an exhausted fast reaction is in general competitive with the currently active slower reactions. In other words, (5.1) is only adequate to be used as an equation of state, but is inadequate to be used in the original equations. See (5.10) later.

**Reaction #3 is dormant:** The contribution by reaction #3 to (4.4) is negligible and need not be included in the time period of interest. It is emphasized that reaction #3 being negligible does not mean  $F^3 \approx 0$ . Hence,  $B^2 \approx K_3A$  is *not* valid and must *never* be used. By neglecting  $s_3F^3$  from (4.4), one can show that:

$$(\Delta H_1 - \Delta H_2)A + (\Delta H_1 - 2\Delta H_2)B + C \approx \text{Constant}. \quad (5.2)$$

which is a (temporary) conservation law. An astute investigator will be able to attribute the physical meaning of “conservation of total energy” to (5.2). If one were interested in the reaction system over a time period of the order of hours, reaction #3 would not be negligible and (5.2) would not be valid.

**The Simplified Model:** The procedures recommended by Williams<sup>[1]</sup> to follow-up the partial-equilibrium approximation proceeds as follows. First, one of the ODE in the system of equations is used to eliminate  $F^1$  from the rest of the equations. For example, (4.5b) can be used to

eliminate  $F^1$  from (4.5a) and (4.5c). These two equations are then supplemented by (5.1) differentiated with respect to time. The simplified model is obtained by solving for  $dA/dt$ ,  $dB/dt$  and  $dC/dt$  from these three equations. We obtain:

$$\frac{dA}{dt} \approx \frac{K_1}{K_1 + 4A} F^2 - \frac{3K_1}{K_1 + 4A} F^3, \quad (5.3a)$$

$$\frac{dB}{dt} \approx \frac{2A}{K_1 + 4A} F^2 - \frac{6A}{K_1 + 4A} F^3, \quad (5.3b)$$

$$\begin{aligned} \frac{dC}{dt} \approx & [\Delta H_2 - \Delta H_1 \left( \frac{K_1 + 2A}{K_1 + 4A} \right)] F^2 \\ & + [\Delta H_3 + \Delta H_1 \left( \frac{2(K_1 + A)}{K_1 + 4A} \right)] F^3. \end{aligned} \quad (5.3c)$$

Note that either (5.3a) or (5.3b) can be replaced by the algebraic equation of state, (5.1). Since  $F^1$  does not appear in this simplified model, this system of ODE is no longer stiff (regardless of how large  $k_1$  is). It can easily be verified that its solution satisfies (5.2) when  $(\Delta H_1 - 3\Delta H_2 - \Delta H_3)F^3$  is negligibly small.

**The New Initial Conditions:** The initial conditions at  $t \rightarrow 0^+$  are no longer given by (4.8), since they must satisfy (5.1). A detailed analysis will show that reaction #2 can also be considered dormant in the brief initial transient period. Hence, in addition to (5.2),  $A + 2B$  is also approximately conserved in this period. Using these results, we have:

$$A(0^+) \approx A(0) + 2(B(0) - B(0^+)) = 1.46 \times 10^{-4}, \quad (5.4a)$$

$$B(0^+) \approx \frac{A^2(0^+)}{K_1} = 1.94 \times 10^{-6}. \quad (5.4b)$$

The value  $C(0^+) \approx 301.04$  can be found from (5.2) applied between  $t = 0$  and  $t = 0^+$ .

## 5.2 The Quasi-Steady Approximation

Alternatively, an investigator may choose to proceed with the quasi-steady approximation instead of the partial-equilibrium approximation.



The quasi-steady state approximation requires that certain species be chosen as “radicals.” If  $B$  is chosen to be the radical, we neglect  $dB/dt$  from (4.5b) to yield the following equation of state:

$$F^1 \approx -F^2 + 2F^3. \quad (5.5)$$

Unlike (5.1), this equation is substituted directly into (4.5a) and (4.5c) to eliminate  $F^1$ . We obtain:

$$\frac{dA}{dt} \approx F^2 - 3F^3, \quad (5.6a)$$

$$\begin{aligned} \frac{dC}{dt} \approx & [\Delta H_2 - \Delta H_1]F^2 \\ & + [\Delta H_3 + 2\Delta H_1]F^3, \end{aligned} \quad (5.6b)$$

These equations agree with (5.3a) and (5.3c) *but only in the  $K_1 \gg A$  limit.* The radical,  $B$ , is to be solved from (5.5) in terms of  $A$ .

If  $K_1 \ll A$ , then  $A$  should be chosen as the radical instead, yielding:

$$F^1 \approx (-F^2 + F^3)/2. \quad (5.7)$$

Substituting this equation into (4.5b) and (4.5c) to eliminate  $F^1$ , we obtain: (4.5c) to eliminate  $F^1$ . We obtain:

$$\frac{dB}{dt} \approx \frac{1}{2}F^2 - \frac{3}{2}F^3, \quad (5.8a)$$

$$\begin{aligned} \frac{dC}{dt} \approx & [\Delta H_2 - \frac{1}{2}\Delta H_1]F^2 \\ & + [\Delta H_3 + \frac{1}{2}\Delta H_1]F^3, \end{aligned} \quad (5.8b)$$

These equations agree with (5.3a) and (5.3c) *but only in the  $K_1 \ll A$  limit.* The radical,  $A$ , is to be solved from (5.7) in terms of  $B$ .

Whenever  $K_1 = O(A)$ , the quasi-steady approximation simply cannot be used<sup>[12],[13]</sup>.

According to this presentation, the quasi-steady approximation is seen to be a special case of the partial-equilibrium approximation. See §5.4 later.

### 5.3 How Good Are These Results?

The analytical results obtained above are only the leading order term of an asymptotic theory valid in the limit of  $k_1 \rightarrow \infty$ . How good are they for the “real” problem at hand? For the example problem, the small dimensionless parameter  $\epsilon$  for an asymptotic theory turns out to be either  $k_2 K_2 / k_1 K_1$  or  $k_3 / (k_1 K_2^2)$ , whichever is larger. For the given rate data, we have  $\epsilon = k_2 K_2 / k_1 K_1 \approx 10^{-1}$ , which is barely adequate to provide one significant figure in the answers. More seriously, if the order of magnitudes of the initial data  $A(0)$  and  $B(0)$  are significantly different from (4.8), these asymptotic results may be totally misleading.

### 5.4 The Exhausted Fast Reaction Rate

We have shown that the equation of state obtained by the partial-equilibrium approximation, (5.1), must not be substituted directly into the original equations because it has inadequate accuracy, while the equation of state obtained by the quasi-steady approximation, (5.5) or (5.7), can be more freely used—with the caveat that its validity depends on the relative magnitude of  $A$  versus  $K_1$ . The question is: can a better approximation be found for  $F^1$  for large time than either (5.1), (5.5) or (5.7)?

Differentiating  $F^1$  with respect to time, we obtain:

$$\begin{aligned} \frac{dF^1}{dt} &= k_1 \left( 2A \frac{dA}{dt} - K_1 \frac{dB}{dt} \right) \\ &= -k_1 (K_1 + 4A) [F^1 - F_\infty^1], \end{aligned} \quad (5.9a)$$

where

$$F_\infty^1 = -\frac{K_1 + 2A}{K_1 + 4A} F^2 + \frac{2(K_1 + A)}{K_1 + 4A} F^3. \quad (5.9b)$$

It is now clear what  $F^1$  does as time marches on. Initially,  $F^1$  decays exponentially with characteristic time scale  $O(|\tau(1)|)$ , but eventually it follows  $F_\infty^1$  which evolves with a slower time scale. The long time asymptotic solution of (5.9a) is, for  $t \gg O(|\tau(1)|)$ :

$$F^1 \approx F_\infty^1 + \tau(1) \frac{d}{dt} F_\infty^1 + \dots, \quad (5.10)$$

where

$$\tau(1) = -\frac{1}{k_1 (K_1 + 4A)}. \quad (5.11)$$

In other words, the leading approximation for  $F^1$  is  $F_\infty^1$  when reaction #1 is exhausted. If  $F^1 \approx F_\infty^1$  is substituted *directly* into (4.5a) and (4.5c), we will indeed recover (5.3a) and (5.3c), the partial-equilibrium results obtained earlier. Hence,  $F^1 \approx F_\infty^1$  is valid without restriction on the relative magnitudes of  $K_1$  and  $A$ ; it is thus a superior equation of state than either (5.1), (5.5) or (5.7), and agrees with them in the appropriate limits.

## 6 The Theory of CSP

The present section explains the CSP procedures and provides intuitive justifications for their validity.

### 6.1 Observations on the Conventional Methodology

The most important information needed by the conventional methodology is the speed ranking of the reactions and the identification of the CSP radicals. Once the fast reactions are somehow identified, and the radicals chosen, the partial-equilibrium and the quasi-steady approximations are available to make further progress—with appropriate caution on the unreliability of the latter. The derivation presented in §5.4 is a new and different way to make progress—it does not need to identify the radical and it clearly yields the most accurate equation of state,  $F^1 \approx F_\infty^1$ . All it needs is assurance that reaction #1 is the fastest.

The theory of CSP provides a systematic way to identify the fast reactions. In addition, it generalizes the procedures in §5.4 to find the exhausted fast reaction rates for massively complex reaction systems.

### 6.2 Basis Vectors

The vector  $\mathbf{g}$  contains all the physics of the problem, and is usually given by the investigator formulating the problem using the physical representation, (2.2).

In general, an  $N$ -dimensional vector may be expressed in terms of any set of  $N$  linearly independent basis vectors<sup>[14]</sup>. CSP exploits the theoretician's prerogative to express  $\mathbf{g}$  in an *alternative representation*, and look for basis vectors with special properties.

Let  $\mathbf{a}_i(t)$ ,  $i = 1, 2, \dots, N$ , be a set of  $N$  linearly independent column basis vectors. The set of inverse row basis vectors,  $\mathbf{b}^i(t)$ ,  $i = 1, 2, \dots, N$ , can be computed from the orthonormal relations:

$$\mathbf{b}^i \odot \mathbf{a}_j = \delta_j^i, \quad i, j = 1, 2, \dots, N, \quad (6.1)$$

where  $\odot$  is the dot product operator of the  $N$ -dimensional vector space. The column vector  $\mathbf{g}$  can now be expressed as:

$$\mathbf{g} = \sum_{i=1}^N \mathbf{a}_i f^i, \quad (6.2)$$

where

$$f^i \equiv \mathbf{b}^i \odot \mathbf{g} = \sum_{r=1}^R B_r^i F^r, \quad i = 1, 2, \dots, N, \quad (6.3)$$

and

$$B_r^i \equiv \mathbf{b}^i \odot \mathbf{s}_r, \quad i = 1, 2, \dots, N. \quad (6.4)$$

Each of the additive terms in (6.2) represents a *reaction mode*, or simply *mode*. The *amplitude* and *direction* of the  $i$ -th mode are  $f^i$  and  $\mathbf{a}_i$ , respectively. Eventually, CSP provides an algorithm to find the “best” set of basis vectors for the derivation of the simplified models.

The physical representation of  $\mathbf{g}$  uses the physically meaningful (and time-independent) stoichiometric vectors as the default column basis vectors. For our example, the default set is:

$$\mathbf{a}_1 = \mathbf{s}_1 = [-2, \quad 1, \quad \Delta H_1]^T, \quad (6.5a)$$

$$\mathbf{a}_2 = \mathbf{s}_2 = [-1, \quad 1, \quad \Delta H_2]^T, \quad (6.5b)$$

$$\mathbf{a}_3 = \mathbf{s}_3 = [1, \quad -2, \quad \Delta H_3]^T. \quad (6.5c)$$

Using this set, the inverse row vectors can easily be computed:

$$\mathbf{b}^1 = [2\Delta H_2 + \Delta H_3, \quad \Delta H_2 + \Delta H_3, \quad 1]/H, \quad (6.6a)$$

$$\mathbf{b}^2 = [-2\Delta H_1 - \Delta H_3, \quad -\Delta H_1 - 2\Delta H_2, \quad -3]/H, \quad (6.6b)$$

$$\mathbf{b}^3 = [-\Delta H_1 + \Delta H_2, \quad -\Delta H_1 + 2\Delta H_2, \quad -1]/H, \quad (6.6c)$$

where

$$H \equiv \Delta H_1 - 3\Delta H_2 - \Delta H_3. \quad (6.6d)$$

Using the given input numerical data, we have:

$$H = 10^3 \text{cc-}^\circ K/\text{mole}. \quad (6.7)$$

In spite of this quite respectable dimensional value,  $H$  is actually very nearly "zero," because it is a small number in comparison to  $\Delta H_1$ ,  $\Delta H_2$  and  $\Delta H_3$ . For "sufficiently small"  $H$ , an alternative  $\mathbf{a}_3$  must be provided. We shall take advantage of  $H \neq 0$  here and proceed with caution.

It is straightforward to verify that at  $t = 0$ , we have:

$$f^1 = \mathbf{b}^1 \odot \mathbf{g} = F^1 = 2.14 \times 10^{-4} \text{mole/cc-second}, \quad (6.8a)$$

$$f^2 = \mathbf{b}^2 \odot \mathbf{g} = F^2 = 1.39 \times 10^{-5} \text{mole/cc-second}, \quad (6.8b)$$

$$f^3 = \mathbf{b}^3 \odot \mathbf{g} = F^3 = -1.19 \times 10^{-8} \text{mole/cc-second}. \quad (6.8c)$$

### 6.3 The Speed Ranking of the Modes

Differentiating (6.3) with respect to time along a solution trajectory  $\mathbf{y}(t)$ , we obtain:

$$\frac{df^i}{dt} = \sum_{j=1}^N \Lambda_j^i f^j, \quad i = 1, 2, \dots, N, \quad (6.9)$$

where

$$\Lambda_j^i \equiv \left[ \frac{d\mathbf{b}^i}{dt} + \mathbf{b}^i \odot \mathbf{J} \right] \odot \mathbf{a}_j, \quad i, j = 1, 2, \dots, N, \quad (6.10a)$$

$$\mathbf{J} \equiv \frac{\partial \mathbf{g}}{\partial \mathbf{y}} = N \times N \text{ Jacobian matrix}. \quad (6.10b)$$

The non-linear nature of the original problem is manifested by the fact that  $\mathbf{J}$  is in general not a constant matrix. At any moment in time, the eigen-values of  $\mathbf{J}$  can be computed. For problems arising from chemical kinetics, they are usually essentially real—when the problems are of the boundary-layer type. The reciprocal of an eigen-value, called the *time scale*, has the dimension of time, and shall be denoted by  $\tau(i)$ . Ordering them in increasing magnitudes, we have:

$$|\tau(1)| < \dots < |\tau(i)| < \dots < |\tau(N)|, \quad (6.11)$$

which provides an approximate speed ranking of the "eigen-modes."

The question what is an ideal set of basis vectors now has an obvious answer: *ideal basis vectors* should diagonalize  $\Lambda_j^i$ , thereby uncoupling all the

modes. This is the standard strategy for analyzing linear problems, but it obviously needs some modifications for non-linear problems because there is no finite algorithm to diagonalize  $\Lambda_j^i$ . A full discussion of this subtle point will be given in a future paper. When the set of basis vectors used is non-ideal, the modes are coupled, and each mode will *not* have a distinct characteristic time scale. As shown in our example in §5.4, the fastest mode  $F^1$  evolves with its own characteristic time scale  $|\tau(1)|$  only initially. As it becomes exhausted, it eventually follows  $F_\infty^1$  which evolves with the characteristic time scales of the slower modes. This *mode mixing* is the price we pay for not diagonalizing  $\Lambda_j^i$ , and is an intrinsic issue of non-linearity which must be dealt with: the fast modes behave as slow modes when they are near exhaustion. Viewed in this light, the task of deriving simplified models is reduced to finding basis vectors such that the fast modes mix with the slow modes as little as possible. From the pragmatic point of view, however, it is not really necessary to uncouple all the modes; it will be sufficient to uncouple the fast modes from the slow modes approximately—so that the residual coupling can be neglected in accordance with some user-specified accuracy threshold. Mode mixing among the fast modes or among the slow modes causes no difficulty and can be tolerated.

## 6.4 The Classification of Fast and Slow Modes

First of all, we need a more precise classification of fast and slow modes. Usually, an investigator has a definite idea on the desired time resolution  $\Delta t$  of the solutions—events whose time scales are below  $\Delta t$  are not of interest. Hence, the group of  $M$  modes which satisfy:

$$|\tau(m)| < \Delta t, \quad m = 1, 2, \dots, M, \quad (6.12)$$

are considered *fast modes*, and all others are the *slow modes*. The fastest group of active slow modes are the *rate-controlling modes*. Slow modes with negligible amplitudes are called *dormant modes*.

If one is interested in all time scales, then  $\Delta t = \tau(M + 1)$ . When time is measured in units of  $\Delta t$ , the fast modes should all be nearly exhausted. We shall deal with a precise definition of exhaustion later. In §5.4, we showed how to obtain the “asymptotic” large time solution for  $F^1$ . We shall generalize the procedure to an arbitrary fast mode below.

## 6.5 The CSP Refinement Strategy

CSP does not attempt to diagonalize  $\Lambda_j^i$ . It assumes that at any moment in time an intelligent set of trial basis vectors is available, and provides an algorithm to refine it. The strategy is to provide a systematic, programmable algorithm which generates a new  $\Lambda_j^i$  which is more block-diagonal than before.

For non-linear problems, the eigen-vectors of  $\mathbf{J}$  are time-dependent, and thus they do not diagonalize  $\Lambda_j^i$ . They are, however, excellent trial basis vectors. As demonstrated in the previous sections, the conventional method uses the default stoichiometric vectors and requires a good guess of the speed ranking of the modes.

The CSP theory uses the ratio

$$\epsilon_M(t) = \left| \frac{\tau(M)}{\tau(M+1)} \right| \quad (6.13)$$

as a small dimensionless parameter, and develops the refinement algorithm by an asymptotic analysis in the small  $\epsilon_M$  limit. Physically,  $\epsilon_M$  is a measure of the *time scale separation* of the fast and slow modes. Each application of the CSP refinement procedure will depress the magnitude of the off-diagonal blocks of  $\Lambda_j^i$  by  $O(\epsilon_M)$ .

## 6.6 The CSP Refinement Procedure

We shall assume that at any moment in time on a solution trajectory, the value of  $M$  is known, and a set of trial basis vectors for the fast modes are given:

$$\mathbf{a}_m, \mathbf{b}^m, \quad m = 1, 2, \dots, M. \quad (6.14)$$

With only the fast basis vectors available, we can compute for the  $M \times M$  upper-left block of  $\Lambda_j^i$ , denoted by  $\omega_n^m$ :

$$\omega_n^m \equiv \Lambda_n^m = \left( \frac{d\mathbf{b}^m}{dt} + \mathbf{b}^m \odot \mathbf{J} \right) \odot \mathbf{a}_n, \quad m, n = 1, 2, \dots, M. \quad (6.15)$$

The inverse of  $\omega_n^m$  shall be denoted by  $\tau_n^m$ :

$$\sum_{n'=1}^M \omega_n^m \tau_n^{n'} = \sum_{n'=1}^M \tau_n^m \omega_n^{n'} = \delta_n^m, \quad m, n = 1, 2, \dots, M. \quad (6.16)$$

We shall mark the refined basis vectors and all entities evaluated with refined basis vectors by either a superscript or a subscript o, or both.

To refine the  $\mathbf{b}^m$  row vectors, we use the so-called *step #1* procedure:

$$\mathbf{b}_o^m = \sum_{n=1}^M \tau_n^m \left( \frac{d\mathbf{b}^n}{dt} + \mathbf{b}^n \odot \mathbf{J} \right), \quad m = 1, 2, \dots, M, \quad (6.17a)$$

$$\mathbf{a}_m^o = \mathbf{a}_m, \quad m = 1, 2, \dots, M. \quad (6.17b)$$

The *step #1* procedure depresses the upper-right  $M \times (N - M)$  block of  $\Lambda_j^i$ —it makes the fast modes “purer” by weakening their couplings with the slow modes. To refine the  $\mathbf{a}_m$  column vectors, we use the so-called *step #2* procedure::

$$\mathbf{b}_o^m = \mathbf{b}^m, \quad m = 1, 2, \dots, M, \quad (6.18a)$$

$$\mathbf{a}_m^o = \sum_{n=1}^M \left( -\frac{d\mathbf{a}_n}{dt} + \mathbf{J} \odot \mathbf{a}_n \right) \tau_m^n, \quad m = 1, 2, \dots, M. \quad (6.18b)$$

The *step #2* procedure depresses the lower-left  $(N - M) \times M$  block of  $\Lambda_j^i$ —it makes the slow modes purer. Note that at each refinement step the orthonormality condition is always satisfied. These two steps may be performed singly, or in tandem in any order, or recursively any number of times—*provided the most current  $\tau_n^m$  is used always*. This refinement procedure is mathematically equivalent to that presented in Lam and Goussis<sup>[10]</sup>, the difference being that in this formulation the slow basis vectors are not involved. If the time derivative terms in (6.17a) and (6.18b) were omitted, the procedure would be identical to the so-called *Mises Power Method* for finding eigen-vectors associated with the largest eigen-values (See Carnahan, Luther and Wilkes<sup>[15]</sup>). In essence, by allowing mode mixing among the fast modes, CSP extends the Mises Power Method to compute the next iterant for the fast basis vectors. Since the time scales of the fast modes are all faster than the current time scale, the time derivative terms are always small corrections.

In practice, the first guess of the trial basis vectors is usually time-independent. The subsequent refined sets will in general be time-dependent because they are, by construction,  $\mathbf{y}$ -dependent. In any case, their time derivatives can be evaluated accordingly. In a computer program, these time derivatives can be evaluated approximately using either stored or predicted data already available in the integration routine. Such programming issues, however, are beyond the scope of this paper.



## 6.7 The Fast Subspace Projection Matrix

We can form a  $N \times N$  matrix  $\mathbf{Q}(M)$  as follows:

$$\mathbf{Q}(M) \equiv \sum_{m=1}^M \mathbf{a}_m \mathbf{b}^m, \quad (6.19)$$

and call it the *fast subspace projection matrix*. When evaluated with refined basis vectors, it will be denoted by  $\mathbf{Q}_o^\circ(M)$ .

Any column vector  $\mathbf{u}$  or row vector  $\mathbf{v}$  can be decomposed into its fast and slow components using either  $\mathbf{Q}(M)$ ,  $\mathbf{Q}_o(M)$  or  $\mathbf{Q}_o^\circ(M)$ . Using  $\mathbf{Q}_o^\circ(M)$ , we obtain:

$$\mathbf{u} = \mathbf{u}_o^{\circ, fast}(M) + \mathbf{u}_o^{\circ, slow}(M), \quad (6.20a)$$

$$\mathbf{v} = \mathbf{v}_o^{\circ, fast}(M) + \mathbf{v}_o^{\circ, slow}(M), \quad (6.20b)$$

where

$$\mathbf{u}_o^{\circ, fast}(M) \equiv \mathbf{Q}_o^\circ(M) \odot \mathbf{u}, \quad (6.21a)$$

$$\mathbf{u}_o^{\circ, slow}(M) \equiv (\mathbf{I} - \mathbf{Q}_o^\circ(M)) \odot \mathbf{u}, \quad (6.21b)$$

$$\mathbf{v}_o^{\circ, fast}(M) \equiv \mathbf{v} \odot \mathbf{Q}_o^\circ(M), \quad (6.21c)$$

$$\mathbf{v}_o^{\circ, slow}(M) \equiv \mathbf{v} \odot (\mathbf{I} - \mathbf{Q}_o^\circ(M)). \quad (6.21d)$$

We can decompose  $\mathbf{Q}(M)$  into its  $M$  components:

$$\mathbf{Q}(M) = \sum_{m=1}^M \mathbf{Q}_m, \quad (6.22)$$

where

$$\mathbf{Q}_m \equiv \mathbf{a}_m \mathbf{b}^m, \quad m = 1, 2, \dots, M. \quad (6.23)$$

We shall call  $\mathbf{Q}_m$  the *fast mode projection matrix* of the  $m$ -th mode.

The *radical pointer* of the  $m$ -th mode,  $Q_m(i)$ , is given by<sup>[12]</sup>:

$$Q_m(i) \equiv \text{the } i\text{-th diagonal element of } \mathbf{Q}_m, \quad i = 1, 2, \dots, N. \quad (6.24)$$

Note that  $Q_m(i)$  is dimensionless, and its sum over all  $N$  components is 1.0. Geometrically,  $Q_m(k)$  is a measure of the projection of the  $k$ -th unit vector

in the  $m$ -th mode. Hence, whenever  $Q_m(k)$  is not a small number, species  $k$  is said to be a CSP radical.

The *fast reaction pointer* of the  $m$ -th mode,  $P_m(r)$ , is given by:

$$P_m(r) \equiv (\mathbf{s}_r)^{-1} \odot \mathbf{Q}_m \odot \mathbf{s}_r, \quad r = 1, 2, \dots, R, \quad (6.25)$$

which is a dimensionless number nominally of order unity. Here,  $(\mathbf{s}_r)^{-1}$  is a set of row vectors orthonormal to the  $\mathbf{s}_r$  set of (linearly independent) column vectors. Physically,  $P_m(r)$  is a measure of the projection of the  $r$ -th stoichiometric vector in the  $m$ -th mode. Whenever  $P_m(r)$  is not a small number, the  $r$ -th reaction is said to be a fast reaction.

## 6.8 The Main CSP Results

Using the available refined basis vectors, the original system of ODE's becomes:

$$\frac{dy}{dt} = \mathbf{g}_o^{o,fast}(M) + \mathbf{g}_o^{o,slow}(M), \quad (6.26)$$

where

$$\mathbf{g}_o^{o,fast}(M) = \mathbf{Q}_o^o(M) \odot \mathbf{g} = \sum_{r=1}^R \mathbf{s}_{o,r}^{o,fast} F^r \quad (6.27a)$$

$$= \sum_{r=1}^R \mathbf{a}_m^o f_o^m, \quad (6.27b)$$

$$\mathbf{s}_{o,r}^{o,fast} = \mathbf{Q}_o^o(M) \odot \mathbf{s}_r = \sum_{m=1}^M \mathbf{a}_m^o B_{o,r}^m, \quad r = 1, 2, \dots, R, \quad (6.27c)$$

$$f_o^m = \mathbf{b}_o^m \odot \mathbf{g} = \sum_{r=1}^R B_{o,r}^m F^r, \quad m = 1, 2, \dots, M, \quad (6.27d)$$

$$B_{o,r}^m \equiv \mathbf{b}_o^m \odot \mathbf{s}_r, \quad m = 1, 2, \dots, M, \quad (6.27e)$$

and

$$\mathbf{g}_o^{o,slow}(M) = (\mathbf{I} - \mathbf{Q}_o^o(M)) \odot \mathbf{g} = \sum_{r=1}^R \mathbf{s}_{o,r}^{o,slow} F^r, \quad (6.28a)$$

$$\mathbf{s}_{o,r}^{o,slow} = (\mathbf{I} - \mathbf{Q}_o^o(M)) \odot \mathbf{s}_r = \mathbf{s}_r - \sum_{m=1}^M \mathbf{a}_m^o B_{o,r}^m, \quad (6.28b)$$

$$r = 1, 2, \dots, R.$$

We shall call  $\mathbf{s}_{o,r}^{o,slow}$  and  $\mathbf{s}_{o,r}^{o,fast}$  the *effective stoichiometric vectors* of the  $r$ -th reaction.

The unrefined fast mode amplitude  $f^m$  satisfies:

$$\frac{df^m}{dt} = \sum_{n=1}^M \omega_n^m (f^n - f_\infty^n), \quad m = 1, 2, \dots, M, \quad (6.29)$$

where

$$f_\infty^m \equiv (\mathbf{b}^m - \mathbf{b}_o^m) \odot \mathbf{g} = f^m - f_o^m \quad (6.30a)$$

$$= -\mathbf{b}_o^m \odot \sum_{r=1}^R \mathbf{s}_r^{slow} F^r, \quad m = 1, 2, \dots, M, \quad (6.30b)$$

and  $\omega_n^m$  in (6.29) and  $\mathbf{s}_r^{slow}$  in (6.30b) are evaluated using the trial basis vectors. Equation (6.29) is the generalized version of (5.9a).

Treating (6.29) as a linear equation for  $f^m$ , we can express its solution as the sum of a homogeneous solution and a particular solution:

$$f^m = f_{hom.o.}^m + f_{part.}^m. \quad (6.31)$$

We shall assume that the eigen-values of  $\omega_n^m$  are essentially negative (*i.e.* the fast modes are of the boundary-layer type). The homogeneous solution is responsible for satisfying the initial conditions, and for boundary-layer type problems it becomes exponentially small in time measured in units of  $\tau(M)$ . The total adjustment of  $y$  in this brief time period can be given approximately by:

$$(\Delta y)_{rc} = - \sum_{m,n=1}^M [\mathbf{a}_m \tau_n^m(M) (f^n - f_\infty^n)]_{t=0}, \quad (6.32)$$

derived under the *ad hoc* assumption that  $\mathbf{a}_m \tau_n^m(M)$  is approximately time-independent. Equation (6.32) is called the *radical correction* by Lam<sup>[12]</sup>. For large time ( $t \gg |\tau(M)|$ ),  $f^m \rightarrow f_{part.}^m$ . The asymptotic solution for  $f_{part.}^m$  can be shown to be:

$$f_{part.}^m = f_\infty^m + \sum_{n=1}^M \tau_n^m(M) \frac{df_\infty^n}{dt} + \dots, \quad m = 1, 2, \dots, M. \quad (6.33)$$

If  $\mathbf{g}^{fast}$  evaluated with  $f^m \approx f_{part}^m$ , is considered negligible in comparison to  $\mathbf{g}^{slow}$  according to some user-specified criterion, the following simplified model is obtained:

$$\frac{dy}{dt} \approx \mathbf{g}_o^{o,slow}(M). \quad (6.34)$$

The “initial” conditions for (6.34) at  $t = 0^+$  must satisfy the following approximate equations of state:

$$f_o^m = \mathbf{b}_o^m \odot \mathbf{g} = \sum_{r=1}^R B_{o,r}^m F^r \approx 0, \quad m = 1, 2, \dots, M. \quad (6.35)$$

The radical correction algorithm can be used to enforce this condition as shall be demonstrated later. Note that (6.34) provides  $N$  ODE’s for the  $N$  unknowns, and its solutions are guaranteed to satisfy (6.35) for all  $t > 0^+$  automatically provided (6.35) is satisfied initially and all fast eigen-values of  $\mathbf{J}$  are essentially negative.

## 7 The CSP Method on the Example

We shall step through the example numerically using CSP.

### 7.1 Choosing the Trial Basis Vectors

We assume that at the beginning we have no idea which reaction is fast. The eigen-values  $\lambda(i)$  and eigen-vectors of  $\mathbf{J}$  at  $t = 0$  can be computed numerically. We have:

$$\lambda(1) = -1.27 \times 10^2/\text{second}, \quad (7.1a)$$

$$\lambda(2) = -0.173/\text{second}, \quad (7.1b)$$

$$\lambda(3) = 0.00/\text{second}, \quad (7.1c)$$

indicating that there is a fast mode with time scale of the order of  $10^{-2}$  seconds, followed by a slower mode with time scale of the order of about  $10^1$  seconds. The right (column) eigen-vectors  $\alpha_i$  and left (row) eigen-vectors  $\beta^i$ , ranked in order of decreasing speed, are:

$$\alpha_1 = [-1.90, \quad 0.993, \quad 1.87 \times 10^4]^T, \quad (7.2a)$$

$$\alpha_2 = [-0.960, \quad -2.46 \times 10^{-2}, \quad -0.901 \times 10^5]^T, \quad (7.2b)$$

$$\alpha_3 = [0.000, \quad 0.000, \quad 1.00]^T, \quad (7.2c)$$

and

$$\beta^1 = [-2.46 \times 10^{-2}, \quad 0.960, \quad 0.00], \quad (7.3a)$$

$$\beta^2 = [-0.993, \quad -1.90, \quad 0.000], \quad (7.3b)$$

$$\beta^3 = [-0.890 \times 10^5, \quad -1.89 \times 10^5, \quad 1.00]. \quad (7.3c)$$

These may be used as our time-independent trial basis vectors for  $t \geq 0$  but they diagonalize  $\Lambda_j^i$  only at  $t = 0$ . Since our time resolution of interest is in seconds, only the first mode can be considered fast. Hence,  $M = 1$ .

Alternatively, we can use the stoichiometric vectors of the three reactions as our trial basis vectors (*i.e.* the default set in §6.2). Since they are time-independent,  $\Lambda_j^i$  is easily computed:

$$\Lambda_j^i = \begin{pmatrix} -1.16 \times 10^2 & -1.13 \times 10^2 & 2.23 \times 10^2 \\ -1.12 \times 10^1 & -1.11 \times 10^1 & 2.21 \times 10^1 \\ 0.216 \times 10^{-2} & 0.208 \times 10^{-2} & -0.408 \times 10^{-2} \end{pmatrix}. \quad (7.4)$$

This matrix has significant off-diagonal terms for all  $t$ . Nevertheless, its diagonal elements can be used to estimate the time scales of the modes, and they indicate that mode #1 (*i.e.* reaction #1) is fastest and its time scale is possibly below the time resolution of interest—suggesting that  $M = 1$ .

In what follows, we shall take  $M = 1$  and choose (6.5a) and (6.6a) as our trial fast basis vectors for  $t \geq 0$ :

$$\mathbf{a}_1 = [-2.00, \quad 1.00, \quad 1.10 \times 10^4]^T, \quad (7.5a)$$

$$\mathbf{b}^1 = [-9.00 \times 10^1, \quad -1.90 \times 10^2, \quad 1.00 \times 10^{-3}]. \quad (7.5b)$$

Using these trial basis vectors, the  $N$  elements of the radical pointer of mode #1 are (taking advantage of the fact that  $H \neq 0$ ):

$$Q_1(1) = 1.80 \times 10^2, \quad Q_1(2) = -1.90 \times 10^2, \quad Q_1(3) = -1.10 \times 10^1. \quad (7.6)$$

Radical pointers computed using trial basis vectors are theoretically unreliable, and this result should be ignored. We shall compute a theoretically reliable radical pointer for mode #1 using the refined basis vectors later. The  $R$  elements of the fast reaction pointer of mode #1 are, as expected:

$$P_1(1) = 1.00, \quad P_1(2) = 0.00, \quad P_1(3) = 0.00. \quad (7.7)$$

confirming that reaction #1 is the fast reaction of the trial fast basis vectors.

## 7.2 Skipping the Rapid Transient Period

Since we are not interested in the rapid transient period which lasts tens of milli-seconds, the main issue now is to find the adjusted initial conditions for the simplified model which governs the slow evolutionary period.

In the rapid transient period,  $\mathbf{y}$  adjusts rapidly in such a way that the amplitude of the fastest mode approaches zero. This adjustment can be computed approximately by the radical correction given by (6.32). For the example here, the amplitude of the fastest mode at  $t = 0$  is  $f^1 = F^1 = 2.14 \times 10^{-4}$ . Making the radical correction using the trial fast basis vectors, we obtain the following adjusted initial condition at  $t = 0^+$ :

$$\mathbf{y}(0^+) = \mathbf{y}(0) + \Delta \mathbf{y}_{rc} = [1.46 \times 10^{-4}, \quad 1.95 \times 10^{-6}, \quad 300.02]^T, \quad (7.8)$$

which yields a much smaller amplitude,  $f^1 = F^1 = -1.36 \times 10^{-7}$ . Note that the relative magnitude of the correction to  $B$  is much larger than those to  $A$  and  $C$ .

## 7.3 The CSP Refinement

Using the trial fast basis vectors (7.5a) and (7.5b), we can decompose  $\mathbf{g}$  into its fast and slow components:

$$\mathbf{g} = \mathbf{g}^{fast} + \mathbf{g}^{slow}, \quad (7.9a)$$

where

$$\mathbf{g}^{fast} = \mathbf{Q}(1) \odot \mathbf{g} = [2.68 \times 10^{-6}, -1.34 \times 10^{-7}, -1.47 \times 10^{-2}]^T, \quad (7.9b)$$

$$\mathbf{g}^{slow} = (\mathbf{I} - \mathbf{Q}(1)) \odot \mathbf{g} = [6.87 \times 10^{-6}, -6.90 \times 10^{-6}, -0.667]^T. \quad (7.9c)$$

In general  $\mathbf{g}^{fast}$  is of the “same order” as  $\mathbf{g}^{slow}$  (component by component), and *its neglect will cause an order unity error* since it was computed using the trial fast basis vector which has never been refined.

The refined fast basis vectors at  $t = 0^+$  are:

$$\mathbf{a}_1^o = [-1.92, \quad 1.00, \quad 1.88 \times 10^4]^T, \quad (7.10a)$$

$$\mathbf{b}_o^1 = [-2.52 \times 10^{-2}, \quad 0.950, \quad 0.000], \quad (7.10b)$$

with  $\tau_o^o(1) = (\mathbf{b}_o^1 \odot \mathbf{J} \odot \mathbf{a}_1^o)^{-1} = -0.788 \times 10^{-2}$  seconds. Note that  $\mathbf{a}_1^o$  and  $\mathbf{b}_o^1$  are quite close to  $\alpha_1$  and  $\beta^1$ , the right and left eigen-vectors of the fastest mode. Note also that  $\mathbf{b}^1$  and  $\mathbf{b}_o^1$  bear no resemblance to each other.

Using the above refined basis vectors for  $t > 0^+$ , the new  $\Lambda_j^i$  is:

$$\Lambda_{j,o}^{i,o} = \begin{pmatrix} -1.27 \times 10^2 & -2.56 \times 10^{-1} & 7.70 \times 10^{-1} \\ 1.03 & -1.65 \times 10^{-1} & 4.95 \times 10^{-1} \\ 3.68 \times 10^{-2} & 9.25 \times 10^{-4} & -2.78 \times 10^{-3} \end{pmatrix}. \quad (7.11)$$

Note that the off-diagonal terms are much smaller than before.

The elements of the new radical pointer using the refined basis vectors of mode #1 are:

$$Q_{o,1}^o(1) = 0.482 \times 10^{-1}, \quad Q_{o,1}^o(2) = 0.952, \quad Q_{o,1}^o(3) = 0.00. \quad (7.12)$$

This (refined) radical pointer is theoretically reliable, and it indicates that  $B$  alone is qualified to be a CSP radical, and that  $C$  must never be so identified. The elements of the new fast reaction pointer are:

$$P_{o,1}^o(1) = 0.906, \quad P_{o,1}^o(2) = 0.941 \times 10^{-1}, \quad P_{o,1}^o(3) = 3.58 \times 10^{-5}, \quad (7.13)$$

again confirming that reaction #1 is the fast reaction.

We can fine tune the initial conditions using the refined basis vectors and apply the radical correction once more. We obtain:

$$\mathbf{y}(0^+) = [1.46 \times 10^{-4} \text{ mole/cc}, 1.89 \times 10^{-6} \text{ mole/cc}, 300.02^\circ \text{K}]^T. \quad (7.14)$$

This correction is mainly on  $B$ , the CSP radical. It is applied again here because (7.8) was computed using the unrefined trial basis vectors and was only a rough correction. It is possible not to use the radical correction if one is willing to numerically integrate the original system of ODE's including  $\mathbf{g}_o^{o,fast}$  and let the rapid transient do the adjustments.

We can now compute the fast and slow components of  $\mathbf{g}$  at  $t = 0^+$ :

$$\begin{aligned} \mathbf{g}_o^{o,fast} &= \mathbf{Q}_o^o(1) \odot \mathbf{g} \\ &= [1.24 \times 10^{-5}, -6.52 \times 10^{-6}, -0.128]^T, \end{aligned} \quad (7.15a)$$

$$\begin{aligned} \mathbf{g}_o^{o,slow} &= (\mathbf{I} - \mathbf{Q}_o^o(1)) \odot \mathbf{g} \\ &= [-5.89 \times 10^{-6}, -1.61 \times 10^{-7}, -0.555]^T. \end{aligned} \quad (7.15b)$$

Equation (7.15a) must be interpreted with care—it should *not* be used to assess whether  $\mathbf{g}^{fast}$  can be neglected in comparison with  $\mathbf{g}^{slow}$ . The proper

order of magnitude estimate of  $\mathbf{g}_o^{o,fast}$  should be made with  $f_o^m \approx f_{o,part.}^m$  as mentioned earlier. The large time asymptotic approximation to the (refined) particular solution is:

$$f_{o,part.}^m \approx f_{o,\infty}^m + \sum_{n=1}^M \tau_{n,o}^{m,o}(M) \frac{df_{o,\infty}^n}{dt} + \dots, \quad m = 1, 2, \dots, M, \quad (7.16)$$

where

$$f_{o,\infty}^m \equiv \sum_{n=1}^M \tau_n^m(M) \frac{df_{\infty}^n}{dt}, \quad n = 1, 2, \dots, M, \quad (7.17)$$

and  $f_{\infty}^n$  was previously defined in (6.30a). In a computer code,  $f_{o,\infty}^m$  can be properly evaluated—the time derivative in (7.16) and (7.17) can be computed either exactly or approximately (*e.g.* using backward finite difference). A rough estimate of the order of magnitude of the exhausted amplitude  $f_o^m$  is:

$$f_o^m \rightarrow f_{o,\infty}^m \approx O\left(\frac{\tau_o^o(M)}{\tau_o^o(M+1)}\right) f_{\infty}^m, \quad m = 1, 2, \dots, M, \quad (7.18)$$

where  $\tau_o^o(M)$  and  $\tau_o^o(M+1)$  are the time scales of the slowest fast mode and the fastest slow mode, respectively.  $\tau_o^o(M)$  can be estimated by the largest reciprocal diagonal element of a  $\Lambda_n^m$  refined at least once.  $\tau_o^o(M+1)$  can be similarly estimated, or it can be taken to be the integration step size selected by an integration routine (*e.g.* RKQC<sup>[16]</sup>). Hence, we have:

$$\mathbf{g}_o^{o,fast} = \sum_{m=1}^M \mathbf{a}_m^o f_o^m \approx O\left[\sum_{m=1}^M \mathbf{a}_m^o \left(\frac{\tau_o^o(M)}{\tau_o^o(M+1)}\right) f_{\infty}^m\right]. \quad (7.19)$$

For the example, we have  $\tau_o^o(1) \approx 0.8 \times 10^{-2}$ ,  $\tau_o^o(2) \approx 0.6 \times 10^1$ , and  $f_{\infty}^1 \approx 6.63 \times 10^{-6}$ . Hence, this rough estimate yields:

$$\mathbf{g}_o^{o,fast} \approx O([-1.6 \times 10^{-8}, \quad 0.8 \times 10^{-8}, \quad 1.6 \times 10^{-4}]^T). \quad (7.20)$$

If all of its components are considered small enough (see next section), we can declare the refined fast mode exhausted—in spite of (7.15a) which does not appear negligible at all—and neglect  $\mathbf{g}_o^{o,fast}$  in comparison to  $\mathbf{g}_o^{o,slow}$  to yield the desired simplified model.

For our example, the amplitude of the exhausted mode #1 is:

$$f_o^1 = \mathbf{b}_o^1 \odot \mathbf{g} = B_{o,1}^1 F^1 + B_{o,2}^1 F^2 + B_{o,3}^1 F^3. \quad (7.21)$$



Neglecting  $f_o^m$  in comparison to the magnitude of the largest positive or negative terms on the right hand side, we have:

$$\sum_{r=1}^R B_{o,r}^1 (F_+^r - F_-^r) \approx 0, \quad (7.22a)$$

or

$$\sum_{r=1}^R B_{o,r}^1 F^r \approx 0. \quad (7.22b)$$

Either is a semi-analytical equation of state—the coefficients  $B_{r,o}^1$  are provided only numerically (at  $t = 0^+$ ):

$$B_{o,1}^1 = \mathbf{b}_o^1 \odot \mathbf{s}_1 = 1.00, \quad (7.23a)$$

$$B_{o,2}^1 = \mathbf{b}_o^1 \odot \mathbf{s}_2 = 0.975, \quad (7.23b)$$

$$B_{o,3}^1 = \mathbf{b}_o^1 \odot \mathbf{s}_3 = -1.92. \quad (7.23c)$$

The terms on the left-hand side of (7.22a) are nearly balanced, and the dominant terms can easily be identified by the *participation index*<sup>[12]</sup>—showing correctly that  $F_+^1 \approx F_-^1$ .

Equation (7.22a) can be used to solve for  $B$ , the identified CSP radical, thus eliminating the need for its ODE. Equation (7.22b) can be used to solve for  $F^1$ , the identified fast reaction, in terms of  $F^2$  and  $F^3$ :

$$F^1 = -0.975F^2 + 1.92F^3, \quad (7.24)$$

which should be compared with (5.1), (5.5) and (5.10), the analytical results valid in the limit  $k_1 \rightarrow \infty$  obtained earlier. See §8 for additional comments.

We can now compute for  $\mathbf{g}_o^{o,slow}$ :

$$\mathbf{g}_o^{o,slow} = \sum_{r=1}^R \mathbf{s}_{o,r}^{o,slow} F^r = \mathbf{s}_{o,1}^{o,slow} F^1 + \mathbf{s}_{o,2}^{o,slow} F^2 + \mathbf{s}_{o,3}^{o,slow} F^3, \quad (7.25)$$

where, at  $t = 0^+$ , we have:

$$\mathbf{s}_{o,1}^{o,slow} = [-0.916, -0.250 \times 10^{-1}, -0.863 \times 10^5]^T \times 10^{-1}, \quad (7.26a)$$

$$\mathbf{s}_{o,2}^{o,slow} = [0.859, 0.234 \times 10^{-1}, 0.809 \times 10^5]^T, \quad (7.26b)$$

$$\mathbf{s}_{o,3}^{o,slow} = [-2.67, -0.728 \times 10^{-1}, -2.52 \times 10^5]^T, \quad (7.26c)$$

and

$$F^1 = -0.975F^2 + 1.92F^3, \quad (7.27a)$$

$$F^2 = -6.76 \times 10^{-6} \text{mole/cc-second}, \quad (7.27b)$$

$$F^3 = 2.61 \times 10^{-8} \text{mole/cc-second}. \quad (7.27c)$$

Which slow reaction(s) ( $F^2$  or  $F^3$  or both) is controlling  $\mathbf{g}_o^{o,slow}$  can easily be identified by the *importance index* introduced in Lam<sup>[12]</sup>.

The above numerical  $\mathbf{s}_{o,r}^{o,slow}$ 's derived for the given problem should be compared with (5.1), (5.3a) and (5.3c), the analytical results obtained earlier. In the  $k_1 \rightarrow \infty$  limit, the CSP-derived analytical results are:

$$[\mathbf{s}_{o,1}^{o,slow}]_{k_1 \rightarrow \infty} = [0, 0, 0]^T, \quad (7.28a)$$

$$[\mathbf{s}_{o,2}^{o,slow}]_{k_1 \rightarrow \infty} = \left[ \frac{K_1}{K_1 + 4A}, \frac{2A}{K_1 + 4A}, \Delta H_2 - \Delta H_1 \frac{K_1 + 2A}{K_1 + 4A} \right]^T, \quad (7.28b)$$

$$[\mathbf{s}_{o,3}^{o,slow}]_{k_1 \rightarrow \infty} = \left[ \frac{-3K_1}{K_1 + 4A}, \frac{-6A}{K_1 + 4A}, \Delta H_3 - \Delta H_1 \frac{2(K_1 + A)}{K_1 + 4A} \right]^T. \quad (7.28c)$$

## 7.4 The User-specified Accuracy Threshold

A perceptive reader would have noticed in (7.20) that the error introduced to  $B$ , the CSP radical, by the neglect of  $\mathbf{g}_o^{o,fast}$  would be the largest. This pessimistic error estimate can be improved by using the radical correction<sup>[12]</sup>.

It can easily be shown that when  $\mathbf{g}_o^{o,fast}$  is neglected and the initial conditions properly adjusted, the solution generated automatically satisfies  $f^m \approx 0$ ,  $m = 1, 2, \dots, M$ . The theory of CSP uses the radical pointer to identify one or more unknowns as CSP radicals for each exhausted fast mode. The resulting  $M$  equations of state can be used to eliminate the ODE's of the  $M$  CSP radicals—using the radical correction. Hence, the accuracy of the CSP radical is controlled by the equations of state, and *not* by the ODE's. A detailed discussion of this subtle point is beyond the scope of this paper. It suffices to state that the error committed in neglecting  $\mathbf{g}_o^{o,fast}$  can be estimated in the conventional way for all other unknowns, but for the CSP radicals the correct estimate is a factor  $\tau(M)/\tau(M+1)$  smaller than indicated when the radical correction is used.

With this caveat, the error of neglecting  $\mathbf{g}_o^{o,fast}$  can be computationally assessed, and fast modes are declared exhausted only when their neglect introduces an error estimated to be below the *user-specified accuracy threshold*,

$y_{error}$ . The *exhaustion criterion*<sup>[12]</sup> for the  $m$ -th fast mode is:

$$|\mathbf{a}_m^o f_{o,\infty}^m \tau(M)| \ll y_{error}, \quad m = 1, 2, \dots, M, \quad (7.29)$$

which must be satisfied component by component.

## 7.5 Exact or Approximate Conservation Laws

In a time period of interest, some reaction modes may be so slow that they can be considered dormant—they can be neglected.

Let the  $(N-M)$ -dimensional slow subspace be spanned by  $\mathbf{a}_J$  and  $\mathbf{b}^J$ ,  $J = M+1, \dots, N$ , the slow trial set which complements the fast trial set of basis vectors. The refinement process described earlier will refine these basis vectors to weaken the coupling between the fast and slow modes. However, within the fast and slow subspaces, the modes are mixed.

One may look for dormant modes among the  $N-M$  slow modes using any reasonable algorithm. If the amplitude  $f_o^K$  of the  $K$ -th (slow) mode satisfies, component by component:

$$|\mathbf{a}_K^o f_o^K \tau(M+1)| \ll y_{error}, \quad (\text{selected } K\text{'s}), \quad (7.30)$$

then it is considered a *dormant mode*.

Exact dormant modes occur frequently in chemical kinetics problems—they are called conservation laws of atomic species. Generations of students have been taught to look for such conservation laws and to use them to advantage in analysis. From the CSP point of view, all exact conservation laws are simply special cases of dormant modes. However, not all dormant modes represent conservation laws.

Dormant modes play no significant role in CSP—inclusion of dormant modes does not cause stiffness. Identification of dormant modes is of interest primarily because they may suggest physically interesting concepts. CSP provides no special technique to find them; we shall assume that they can be somehow found and be identified using (7.30).

Unlike exhausted fast modes, the relation

$$f_o^K = \mathbf{b}_o^K \odot \mathbf{g} \approx 0, \quad (\text{selected } K\text{'s}), \quad (7.31)$$

does *not* produce an equation of state. In the case of conservation law of atomic species, for example,  $\mathbf{b}_o^K \odot \mathbf{g} = 0$  is an identity: zero equals to zero.

However, if  $\mathbf{b}_o^K$  can be expressed in the form:

$$\mathbf{b}_o^K = \theta_{K,o} \frac{\partial \Theta_{K,o}}{\partial \mathbf{y}}, \quad (\text{selected } K\text{'s}), \quad (7.32)$$

where  $\theta_{K,o}$  and  $\Theta_{K,o}$  are scalar functions of  $\mathbf{y}$ , then mode  $\#K$  indeed may represent a conservation law. Lam<sup>[12]</sup> called such  $\Theta_{K,o}$ 's *eligible conserved scalars*, and such modes *holonomic modes*—a name borrowed from classical mechanics<sup>[17]</sup>. At the present time, there is no known method to determine whether a computed slow  $\mathbf{b}_o^K$  is holonomic—except when it is a time-independent constant. All exhausted fast modes are approximately holonomic, with  $\theta_{m,o} = 1$  and  $\Theta_{m,o} \approx f_o^m$ .

Whenever a holonomic  $f_o^K$  is dormant,  $\Theta_{K,o}$  becomes a *conserved scalar* which is an algebraic relation among the unknowns. Unlike equations of state obtained from exhausted fast modes, conserved scalars always contain a free parameter determined by initial conditions. For addition discussion, see Lam<sup>[12]</sup>.

In our example, (7.27c) shows that  $F^3$  is quite small in comparison to  $F^2$ . This observation by no means implies that  $F^3 \approx 0$ —it only means that  $\mathbf{s}_{o,3}^{o,slow} F^3$  can be neglected from (7.25) in this time period. To find the dormant mode, we may use  $(\mathbf{s}_1, \mathbf{s}_2, \boldsymbol{\alpha}_3)$  as our trial basis vectors. The slow mode  $\#3$  will be found to be a dormant mode, with  $\mathbf{a}_3^o = [0, 0, 1]^T$  and  $\mathbf{b}_o^3 = [-0.890 \times 10^5, -1.89 \times 10^5, 1.00]$ . The row vector  $\mathbf{b}_o^3$  will be found numerically to be nearly constant in time, and analytically it can be shown that:

$$\mathbf{b}_o^3 \approx [\Delta H_1 - \Delta H_2, \Delta H_1 - 2\Delta H_2, 1](1 + O(k_3 K_3 / k_1 K_1)). \quad (7.33)$$

In other words, this is approximately an holonomic mode, with  $\theta_{3,o} = 1$  and

$$\Theta_{3,o} = \mathbf{b}_o^3 \odot \mathbf{y} \approx (\Delta H_1 - \Delta H_2)A + (\Delta H_1 - 2\Delta H_2)B + C, \quad (7.34)$$

which can be interpreted as the total energy of the system. Theoretically,  $\Theta_{3,o}$  evolves with time scale of  $O(H/(\Delta H_3 k_3 K_3))$  which is measured in hundreds of seconds; it only *appears* to be a conserved scalar quantity in the time period of  $O(1/(k_2 K_2))$  which is measured in seconds.

## 8 A Stiffness-Related Programming Issue

The *Associative Law of Addition* is one of the fundamental laws of algebra. It states that:

$$(x + y) + z = x + (y + z). \quad (8.1)$$

*It is not generally appreciated that this law is not valid on a finite precision computer.* One can easily confirm this observation by trying  $x = 10^{15}$ ,  $y = -10^{15}$ , and  $z = 1.23$  on a hand calculator.

The numerical violation of the Associative Law of Addition is caused by loss of significant figures in subtracting large numbers or adding large and small numbers. In a chemical kinetics problem involving fast and slow reactions, the evaluation of the vector  $\mathbf{g}$  indeed involves subtraction and addition of large and small numbers. Hence one must pay special attention to the evaluation of  $\mathbf{g}$  inside a computer program.

Mathematically,  $\mathbf{g}$  can in principle be evaluated by any of the following formally identical expressions:

$$\mathbf{g} := \sum_{r=1}^R \mathbf{s}_r F^r, \quad (8.2a)$$

$$\mathbf{g} := \sum_{r=1}^R \mathbf{s}_r F_+^r - \sum_{r=1}^R \mathbf{s}_r F_-^r, \quad (8.2b)$$

$$\mathbf{g} := \sum_{r=1}^M \mathbf{a}_m^o f_o^m + \mathbf{g}_o^{o,slow}, \quad (8.2c)$$

where  $f_o^m$  is given by (6.27d):

$$f_o^m := \sum_{r=1}^R B_{o,r}^m F^r, \quad m = 1, 2, \dots, M, \quad (8.2d)$$

and

$$\mathbf{g}_o^{o,slow}(M) := \sum_{r=1}^R \mathbf{s}_{o,r}^{o,slow} F^r, \quad (8.2e)$$

$$F^r := F_+^r - F_-^r, \quad r = 1, 2, \dots, R. \quad (8.2f)$$

For sufficiently stiff problems, all three evaluations are numerically unreliable. However, (8.2c) can be made reliable by applying CSP concepts as shall be shown presently.

The amount of cancellation in the evaluation of  $f_o^m$  and  $F^r$  can be measured by:

$$\delta f_o^m \equiv \frac{|f_o^m|}{\sum_{r=1}^R (|B_{o,r}^m F_+^r| + |B_{o,r}^m F_-^r|)}, \quad m = 1, 2, \dots, M, \quad (8.3a)$$

$$\delta F^r \equiv \frac{|F^r|}{|F_+^r| + |F_-^r|}, \quad r = 1, 2, \dots, R, \quad (8.3b)$$

which are both dimensionless numbers. Clearly, when either  $\delta f_o^m$  or  $\delta F^r$  is very small, the accuracy of  $f_o^m$  or  $F^r$  so evaluated is suspect. In our example,  $\delta f_o^1$  and  $\delta F^1$  are  $O(k_2 K_2 / (k_1 K_1))$  after the rapid transient period, and—to dramatize the situation—if  $k_2 K_2 / (k_1 K_1) = O(10^{-18})$  then even double-precision arithmetic would be inadequate.

CSP uses (8.2c), but intelligently. When  $f_o^m$  is near exhaustion, CSP provides its leading order asymptotic approximation, (6.33). Since  $f_\infty^m$  is a known function of  $y$ , the needed time derivative can be appropriately evaluated. Hence, whenever  $f_o^m$  has inadequate significant figures as evaluated by (8.2d), (6.33) can be used in its place. In fact, it is recommended that  $f_{o,\infty}^m$  be used (instead of  $f_o^m$ ) to assess whether the  $m$ -th mode should be declared exhausted. In other words, CSP properly recognizes the contribution of  $\mathbf{g}_o^{o,fast}$  to  $\mathbf{g}$  in (8.2c) to be at best a minor correction whenever substantial cancellation occurs in the direct evaluation of  $f_o^m$ .

Similarly, in the evaluation of  $\mathbf{g}_o^{o,slow}$ , all  $F^r$ 's are involved. The values of the exhausted fast  $\delta F^r$ 's will be very small, and the corresponding values of the  $F^r$ 's will be suspect. The theory of CSP provides  $M$  fast reaction pointers to identify  $M$  fast reactions, and their net reaction rates can be solved for from (8.2d) in terms of the rest of the net reaction rates. Hence, the use of potentially inaccurate fast  $F^r$ 's are avoided. In our example, the value of  $F^1$  after the rapid transient periods should *not* be computed from  $F^1 = k_1(A^2 - K_1 B)$ , the theoretically exact expression, but should be evaluated from  $F^1 \approx -(B_{o,2}^1 F^2 + B_{o,3}^1 F^3) / B_{o,1}^1$  instead, the CSP-derived approximation.

The computation of the effective stoichiometric vector of the  $r$ -th reaction,  $\mathbf{s}_{o,r}^{o,slow}$ , involves  $[\mathbf{I} - \mathbf{Q}_o^o(M)]$ , and its dimensionless diagonal elements are obtained by a subtraction process which may lose significant figures. The following artifice has been found successful in eliminating specious errors in the direct evaluation of  $\mathbf{s}_{o,r}^{o,slow}$ : Whenever any diagonal element of this

matrix falls below an appropriate threshold (*e.g.*  $10^{-4}$  for four significant figures calculations), it is replaced by a zero.

## 9 Discussion

The traditional role of a theoretician has always been to simplify seemingly complex problems into their bare elements. Physical insights and intuition are at the root of this process, helped considerably by the methodology of asymptotics when a small parameter is available and can be identified. As a practical matter, asymptotic solutions usually consists of very few terms—the so-called leading order solution is usually all that could be expected because of the massive amount of algebra involved. In §5, the analytical results obtained are formally correct only in the limit of  $k_2 K_2 / (k_1 K_1) \rightarrow 0$ ,  $k_3 / (k_1 K_2^2) \rightarrow 0$ . No assurance of accuracy is provided when applied to problems with  $k_2 K_2 / (k_1 K_1) \approx 0.1$ .

The theory of CSP welcomes physical insights and experience, but is not dependent on them. It uses the eigen-values of  $\mathbf{J}$  to order the trial modes, and provides a refinement procedure to improve the decoupling of the trial fast and slow subspaces. From the viewpoint of CSP, users of conventional asymptotics simply make educated guesses at the fast basis vectors. The special procedures to apply the partial-equilibrium and quasi-steady approximations are just variants of the CSP refinement procedure. In the absence of insights and experience, the conventional methodology cannot get started at all, but CSP can proceed routinely—the eigen-vectors of  $\mathbf{J}$  can always be used as the trial set<sup>[18]</sup>. Most importantly, the refinement procedure can be recursively applied, allowing “higher-order” corrections to be included. The CSP user has the responsibility to specify the threshold of tolerable error  $y_{\text{error}}$ , and CSP makes sure that the error introduced by the neglect of  $\mathbf{g}_o^{o,fast}$  is below threshold. Different simplified models will be generated for different user-specified  $y_{\text{error}}$ ; a lenient threshold will yield a simpler model than a more stringent one.

The method of CSP is a significant advance over the method of *matched asymptotic expansions*<sup>[19]</sup> for boundary-layer type problems. First of all, it can be applied without the need of non-dimensionalizations and identification of small parameters. In essence, CSP exploits the disparity of time scales between the exhausted fast modes and the currently active slower modes, and

the small dimensionless parameter being exploited is  $\epsilon_M$  defined in (6.13). The simplified model is constructed by an iterative procedure; each iteration improves the accuracy of the model by  $O(\epsilon_M)$ . It is important to note that the time derivative term in (6.17a) and (6.18b) *must* be included in the refinement procedures if accuracy beyond “leading order” is desired. The superiority of the CSP approach to the conventional methodology, when applied analytically to simple problems, is clearly demonstrated in §7.3. For massively complex problems, the CSP approach has no peers.

The CSP-derived simplified model remains a system of  $N$  ODE’s which is accompanied by a set of  $M$  equations of state. Theoretically, the solutions of the simplified model automatically satisfy the  $M$  equations of state for  $t \geq 0^+$  if the initial conditions satisfy them at  $t = 0^+$ —assuming that exhausted modes did not become active again. CSP uses all  $N$  ODE’s to march forward in time for all  $N$  components of  $\mathbf{y}$ , and uses the  $M$  equations of state only to apply the radical corrections to prevent the “drifting” of the exhausted fast mode amplitudes.

For each fast mode, CSP provides a radical pointer which identifies the CSP radicals—species which can be solved for from the equation of state. It is extremely important to note that one may *not* arbitrarily select any  $M$  species to be solved for from the  $M$  algebraic equations. In the conventional approach, the algebraic difficulty of solving for the radicals frequently forces additional *ad hoc* approximations. CSP deals with this obstacle again using iteration; the programmable radical correction procedure can be recursively applied to solve for the CSP radicals. In fact, the radical correction should be applied after every integration step to counter the usually larger estimated error of neglecting  $\mathbf{g}_o^{o,fast}$  for the CSP radicals. The refined basis vectors from the previous time step can be used as trial basis vectors for the current time step. In addition, CSP provides a fast reaction pointer for each fast mode, and an algorithm to accurately evaluate the amplitudes of exhausted fast reactions.

The CSP method has no difficulty in identifying dormant modes, but does not provide a method for finding the so-called eligible conserved scalars—except for the simplest case when the row basis vector of the mode in question is found to be time-independent. At the present time, CSP does not take advantage of any conservation laws which may be available.

Trevino *et. al.*<sup>[20],[21]</sup> successfully studied ignition phenomena with the assistance of CSP data. CSP data can also be used to assess sensitivity of so-



lutions with respect to the input rate coefficients<sup>[22]</sup>, and offers an attractive alternative to the conventional method of sensitivity analysis<sup>[23]</sup>.

After mode #2 also becomes exhausted, it can be shown by conventional methodology that  $A$  and  $B$  become time-independent, but  $C$  varies linearly with time when  $HF^3 \neq 0$ . The CSP method *routinely* obtains the simplified model in this period with  $M = 2$ , and the exercise is left to the interested readers.

## References

- [1] Williams, F.A., *Combustion Theory, The fundamental theory of chemically reacting systems*, 2nd edition, Benjamin/Cummings Publ. Co., Menlo Park, Ca., 1985.
- [2] Benson, S. W., "The induction period in chain reactions," *J. Chem. Phys.* **20**, p. 1605, 1952.
- [3] Bowen, J. R., Acrivos, A. and Oppenheim, A. K., "Singular perturbation refinement to quasi-steady state Approximation in chemical kinetics," *Chem. Eng. Sci.* **18**, p. 177, 1963.
- [4] Peters, N., "Numerical simulation of combustion phenomena," Glowinski, R., Larrourou, B and Temem, R., Eds., *Lecture Notes in Physics* **241**, p. 90-109, Springer-Verlag, New York, 1985.
- [5] Peters, N. and Williams F. A., "The asymptotic structure of stoichiometric methane-air Flames", *Combust. Flame*, **68**, pp. 185-207, 1987.
- [6] Aiken, R. C., *Stiff Computation*, Oxford University Press, 1985.
- [7] Lam, S. H., "Singular perturbation for stiff equations using numerical methods", in *Recent Advances in the Aerospace Sciences*, Corrado Casci, Ed., Plenum Press, New York and London, pp. 3-20, 1985.
- [8] Lam, S. H. and Goussis, D. A., "Basic theory and demonstrations of computational singular perturbation for stiff equations", *12th IMACS World Congress on Scientific Computation*, Paris, France, July 18-22, 1988; *IMACS Transactions on Scientific Computing '88, Numerical and*

- Applied Mathematics*, C. Brezinski, Ed., J. C. Baltzer A. G. Scientific Publishing Co., pp. 487-492, November, 1988.
- [9] Lam, S. H. and Goussis, D. A., "Understanding complex chemical kinetics with computational singular perturbation", *Proceedings of the 22nd International Symposium on Combustion*, pp. 931-941, University of Washington, Seattle, Washington, August 14-19, 1988.
- [10] Lam, S. H. and Goussis, D. A., in *Reduced Kinetic Mechanisms and Asymptotic Approximations for Methane-Air Flames*, Chapter 10: "Conventional asymptotics and computational singular perturbation for simplified kinetics modeling," *Lecture Notes in Physics 384*, M. Smooke, Ed., Springer-Verlag, 1992.
- [11] Goussis, D. A. and Lam, S. H., "A study of homogeneous methanol oxidation kinetics using CSP," *Proceedings of the 24th International Symposium on Combustion*, University of Sydney, Sydney, Australia, July 5-10, 1992.
- [12] Lam, S. H., "Using CSP to understand complex chemical kinetics," *Combustion Sci. Tech.*, **89**, pp. 375-404, 1993.
- [13] Trevino, C. and Williams, F.A., "An asymptotic analysis of the structure and extinction of methane-air diffusion flame," *11th International Colloquium on Dynamics of Explosions and Reactive Systems*, Warsaw, Poland, 1987.
- [14] Noble, B. and Daniel, J. W., *Applied Linear Algebra*, Third Edition, Prentice Hall, Inc. 1988.
- [15] Carnahan, B, Luther, H. A. and Wilkes, J. O., *Applied Numerical Methods*, John Wiley and Sons, New York, 1969.
- [16] Press, W. H., Flannery, B. P., Teukolsky, S.A. and Vetterling, W. T., *Numerical Recipes, The Art of Scientific Computing*, Cambridge University Press, Cambridge, 1986.
- [17] Sommerfeld, A., *Mechanics*, Academic Press, N. Y., 1952.

- [18] Maas, U. and Pope, S. B., "Simplifying Chemical Kinetics: Intrinsic Low-Dimensional Manifolds in Composition Space," *Combust. Flame*, **88**, pp. 239-264, 1992.
- [19] Van Dyke, M., *Perturbation Methods in Fluid Mechanics*, Parabolic Press, Stanford, Ca. 1975.
- [20] Trevino, C. and Solorio, F., "Asymptotic Analysis of the High Temperature Ignition of  $CO/H_2/O_2$  Mixtures," *Combust. Flame*, **86**, pp. 285-295, 1991.
- [21] Trevino, C., "Ignition Phenomena in  $H_2 - O_2$  Mixtures," in *Dynamics of Deflagration and Reactive Systems and Flames*, A. L. Kuhl *et. al.*, Ed., *Progress in Aeronautics and Astronautics*, AIAA, 1991.
- [22] Lam, S. H. and Goussis, D. A., "Sensitivity analysis of complex simulations using basis vectors," presented at the 13th IMACS World Congress on Computation and Applied Mathematics, Dublin, July 22-26, 1991.
- [23] Yetter, R. A., Dryer, F. L. and Rabitz, H., "A Comprehensive Reaction Mechanism of Carbon Monoxide/Hydrogen/Oxygen Kinetics," *Combust. Sci. Tech.*, **79**, pp. 97-128, 1991.



